

IITRI Project G-6003
Final Report

GRAPHITE-METAL COMPOSITES

Contract No. NASr-65(09)

Prepared for

Office of Research Grants and Contracts

Code BG

National Aeronautics and Space

Administration

Washington 25, D. C.

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For the Period August 1, 1965 - July 31, 1966

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ABSTRACT

This program has been concerned with the fabrication and characterization of hot pressed metal carbide-graphite composites. Systems incorporating the carbides of titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum or tungsten with compositional ranges of up to 90 wt% have been studied. Processing temperatures were varied from 2600° to 3200°C. The effects of these parameters upon physical and mechanical properties up to 2800°C have been determined.

The studies have shown that dense high strength composites can be obtained through careful choice of materials and fabrication procedure. Needle cokes have been found to be preferable to spherical particle graphite sources in achieving rapid densification. Exceeding the liquification temperature can result in gross loss of the metal phase with subsequent loss of bonding. At the 50 wt% metal level in any system, hot pressing just below the eutectic temperature will produce composites having room temperature strengths of over 10,000 psi. The metal phase enhances ordering of the graphite phase, and improved bonding occurs through liquid phase sintering and/or diffusion bonding.

High temperature behavior is related to the liquification temperature of the particular system. The highest strengths and resistance to deformation at $\geq 2500^{\circ}\text{C}$ has been shown by TaC-C which has the highest carbide-carbon eutectic (3450°C). NbC-C also displays good structural integrity at the high temperatures; this system has the second highest eutectic temperature (3250°C). These along with ZrC-C exhibit maximum flexural strength at 2000°C . Systems having carbide-carbon eutectics or carbide melting points of less than 2800°C do not display this peak; plastic deformation

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is already evident for these systems at 2000°C.

An interesting development during this investigation has been the discovery that an essentially linear relationship exists between electrical resistivity and flexural strengths. This relationship may be useful in predicting the properties and structure of metal carbide-graphite composite system. Preliminary examination suggest good thermal shock resistance for the systems TaC-C, NbC-C, and ZrC-C.

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GRAPHITE-METAL COMPOSITES

I. INTRODUCTION AND SUMMARY

The number of materials which can offer satisfactory performance diminishes rapidly as temperature requirements increase. Carbides and graphite have received increasing attention since they are the most refractory materials known. Composites of these two materials appear attractive in that the carbide offers high strength, and incorporation of graphite results in good thermal shock resistance and in easier machinability.

The earlier investigations in the first year's program¹ had demonstrated that metal carbide-graphite mixtures could be hot pressed into dense composites of high strength. The studies included the following additives in weight percent of metal up to 50%: TiC, ZrC, HfC, NbC, TaC, Mo₂C, B₄C, UC₂ and ThC₂.

During the course of the present work, compositional studies were extended to higher metal contents of near carbide-carbon eutectic compositions. Much of the effort was expended on investigations of systems incorporating niobium carbide or tantalum carbide since these exhibited the greatest potential for high temperature use.

Metal additions which have been investigated are the groups -IVA, -VA, and -VIA metal carbides with the exception of chromium. Vanadium and tungsten carbides were included as type comparisons for groups -VA and -VIA metals.

In the preparation of the various composites, the effects of different fabrication parameters were evaluated. Hot pressing temperatures of up to 3200°C were employed to enhance sintering rates and diffusion. Mechanical properties measurements were conducted at temperatures up to 2800°C and were broadened to include compressive behavior and electrical properties.

The most significant findings in the studies are as follows:

1) The use of flat, platy carbon particles as opposed to spherical cokes yields better densification and bonding in metal carbide-graphite composites. Calcined petroleum coke appears to be a good graphite source.

2) Fabrication at temperatures which exceed the carbide-carbon eutectic or carbide melting point can result not only in significant loss of metal with concomitant lowering of strength, but also in gross segregation of the two phases and formation of large pores. This applies to the following systems: 50 wt% compositions of TiC-C, ZrC-C, VC-C, and near eutectic compositions of NbC-C. However, such liquid formation does not detrimentally affect systems incorporating the carbides of molybdenum or tungsten as 50 wt% metal compositions.

3) Room temperature flexural strengths of over 10,000 psi can be expected for all systems at a metal content of 50 wt%. This supposes, of course, that the processing conditions used are such as to provide optimum densification and bonding.

4) An increase in strength at 2000°C and strength levels of over 10,000 psi at 2500°C exists for all ≥ 50 wt% metal compositions containing tantalum carbide, niobium carbide, hafnium carbide, or zirconium carbide. Composites incorporating the carbide of titanium, vanadium, molybdenum or tungsten exhibit 2000°C strengths which are about the same as those at room temperature; plastic behavior is displayed by these systems at 2500°C.

5) TaC-C and NbC-C compositions having metal contents up to 90 wt% or a volume content of about 75% have been fabricated successfully. Flexural strengths in the $\geq 20,000$ psi range are shown by these composites. Although more plastic deformation in flexure was observed for the carbide matrix materials as compared to graphite matrix bodies, excellent resistance to

deformation under relatively low compressive loads (2000 psi, 2500° - 2650°C) was evident for all compositions.

6) A linear strength-electrical resistivity relationship has been found to hold for metal carbide-graphite composites. This relationship appears to hold regardless of density, processing temperature, wt% metal, grain direction, or carbon source for any particular system. This linearity indicates that strength is directly proportional to particle-to-particle contact of the carbide or eutectic which is the strength providing phase.

II. EXPERIMENTAL PROCEDURE

A number of metal carbide-graphite composites have been hot pressed at temperatures of 2600° to 3250°C. The raw materials used in these fabrications, processing conditions maintained and their effects, and procedures for evaluation of finished composites are discussed in the following sections.

A. Raw Materials

The first year's studies had shown that greater densification and higher strengths were obtained using raw materials of finer particle size. Thus in this year's program both metal and metal carbide powders were obtained as -325 mesh (less than 44 microns), and the calcined petroleum coke (Continental No. 90 coke flour) was screened to the same mesh size. Various suppliers were used for the metal source. The following materials were obtained from the Wah Chang Corporation: niobium, niobium carbide (Grade II), tantalum, tantalum carbide (Grade II), molybdenum, molybdenum carbide, zirconium carbide (reactor grade) and hafnium carbide (reactor grade). Other suppliers and their products are Shieldalloy Corporation: zirconium carbide, vanadium carbide and titanium carbide; Fansteel Metallurgical Corporation: niobium; and, Thermal Dynamics Corporation: tungsten (E-1 flame spray powder).

The range of powder particle sizes and shapes which can exist in "-325 mesh" material are shown in Fig 1. Molybdenum

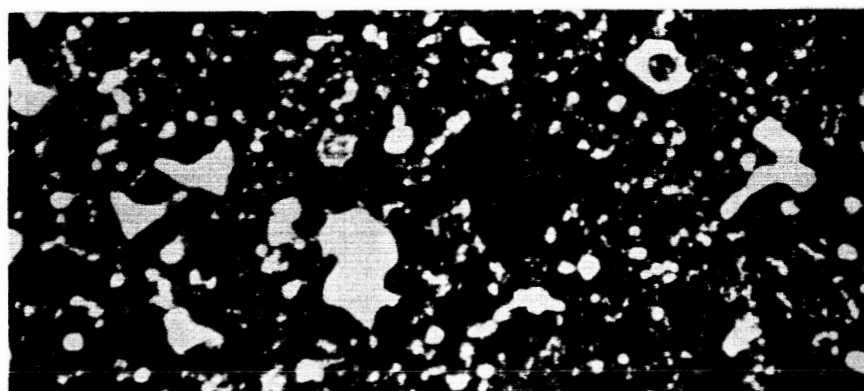
50 μ



(a) ZrC (Wah Chang)



(b) HfC (Wah Chang)



(c) W (Thermal Dynamics)

Fig 1 - PARTICLE SIZE AND SHAPE
OF RAW MATERIALS
(REFLECTED LIGHT, 320 X)

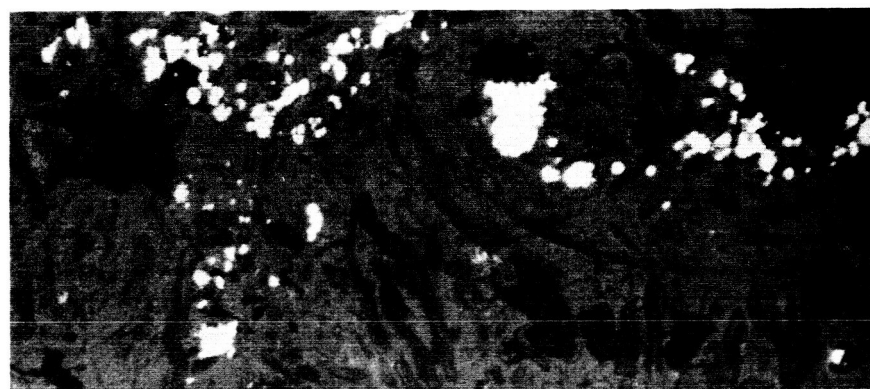
50 μ



(d) Ta (Wah Chang)



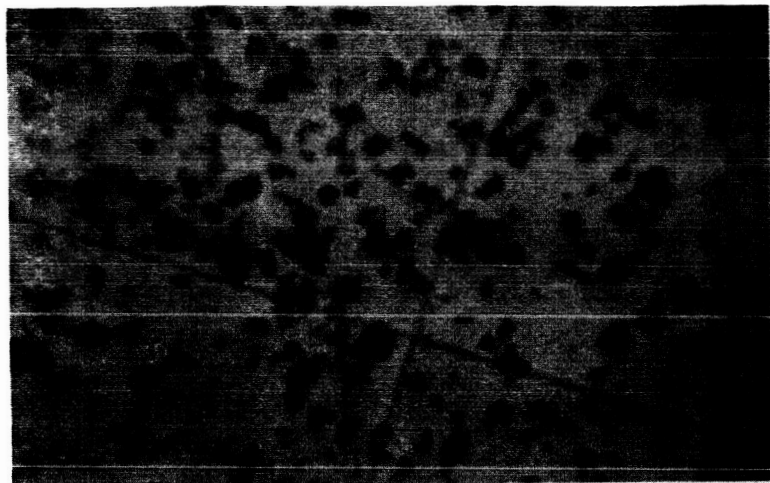
(e) Nb (Fansteel)



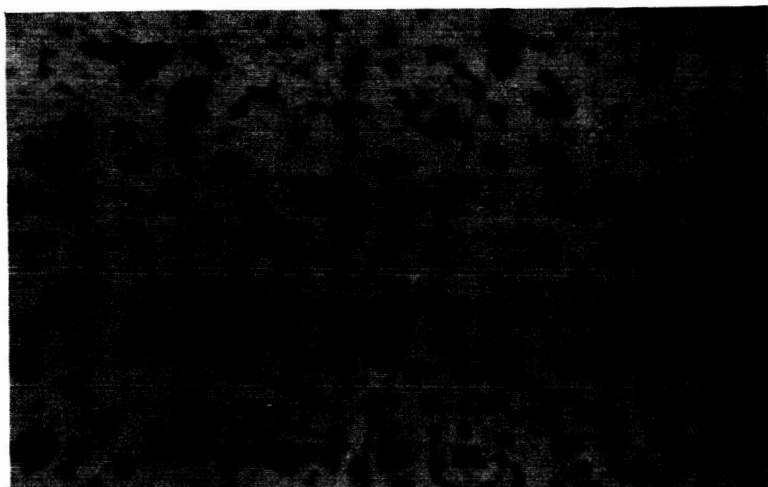
(f) Mo (Wah Chang)

Fig 1 - PARTICLE SIZE AND SHAPE
OF RAW MATERIALS
(REFLECTED LIGHT, 320 X)

50 μ



(g) TaC (Wah Chang)



(h) NbC (Wah Chang)



(i) Calcined Petroleum
Coke

Fig 1 - PARTICLE SIZE AND SHAPE
OF RAW MATERIALS
(TRANSMITTED LIGHT, 360 X)

metal powder is extremely fine with a range of about 2 - 5 microns. In contrast, tantalum and niobium powders were quite coarse and angular in shape; 40 micron particles were common. The carbides of tantalum and niobium were considerably finer (about 10 - 15 microns) than the respective metals. This evaluation has shown the significant differences in material designated <44 microns; additional data will be presented to show that the larger particles can be responsible for poorer bonding due to limited diffusion in composites where graphite is the major phase.

B. Preparation and Fabrication

During the present program, steps were taken to improve and refine the hot pressing procedure. The complete operation was monitored carefully to determine effects of temperature and pressure on the molds and equipment as well as on the carbide-carbon composites. The results of these fabrication experiments are presented below.

1. Modifications

Some changes were introduced into the processing procedure for this year for closer control of processing variables. These changes are as follows:

- 1) Greater care in loading of a mixture into a mold so as to insure homogeneity and avoid segregation of the heavier metal phase.
- 2) Incorporation of a constant pressure device to replace manual pressing for more uniform, continuous loading.
- 3) An improved venting system for the gas purge in the sight tube to minimize the presence of volatiles. These fumes have led to difficulties in pyrometry due to attenuated transmittance.

- 4) Maintenance of pressure and temperature of any hot pressing experiment until ram movement indicated that ultimate density had been attained. Earlier work had been concerned with reaching the pressing temperature, at which point the fabrication was concluded.

The various steps in the processing method, i.e. mixing of components, pressure application rate, and heating rates, were essentially the same as in the first year's work.¹ Compositions were dry blended by roller milling for 16 hours. The initial pressure applied in hot pressing was maintained until a temperature of 2000°C was attained, at which time it was increased to 3000 psi for the remainder of the heating cycle. The pressure was released on the cooling cycle at 2000 psi. The temperature of the pressing (2600° - 3100°C) was attained in approximately one to 1 1/2 hours from room temperature; at this point temperature was maintained until ram movement indicated that ultimate density had been achieved. A diagram of the apparatus appears in Fig 2.

2. Temperature Calibration

An experimental study was conducted early in the program to determine more precisely the temperature of a sample during processing. A run was conducted in which temperature indicated in the sight tube (T_1) and in the actual sample locale (T_2) were monitored simultaneously as shown in Fig 3. The "sample" was a graphite mold plunger with the desired optical and purge gas paths drilled in. A graph (Fig 3a) showing the comparative temperatures reveals a lag in T_2 at the lower temperature during heating. This is to be expected since induction heating occurs from the outside, or skin of the susceptor, inward. At higher temperatures in excess of 2500°C, the lag is less evident and equilibrium seems to be maintained throughout

Scale: 1/4" = 1"

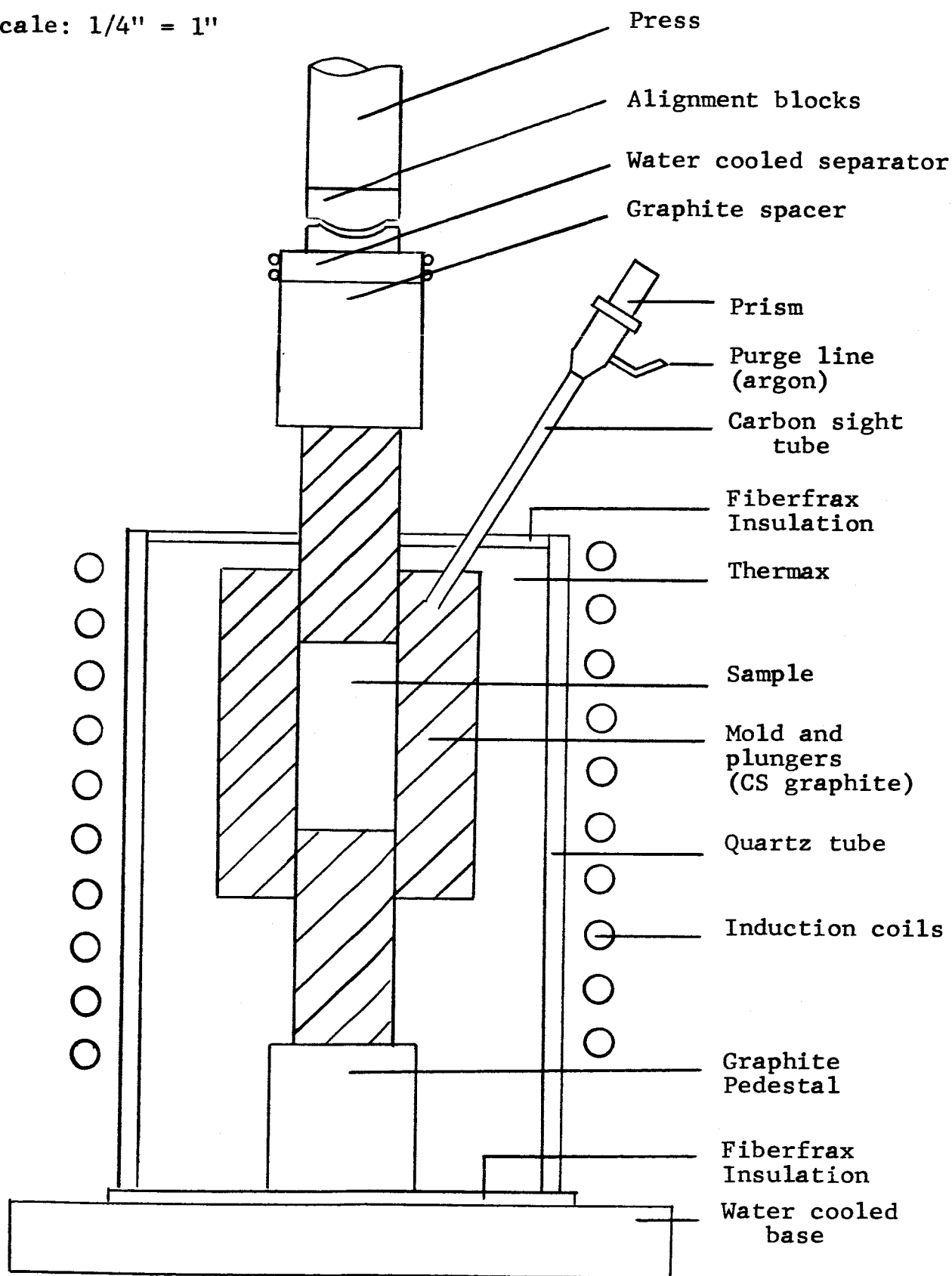


Fig 2 - DIAGRAM OF HOT PRESS APPARATUS

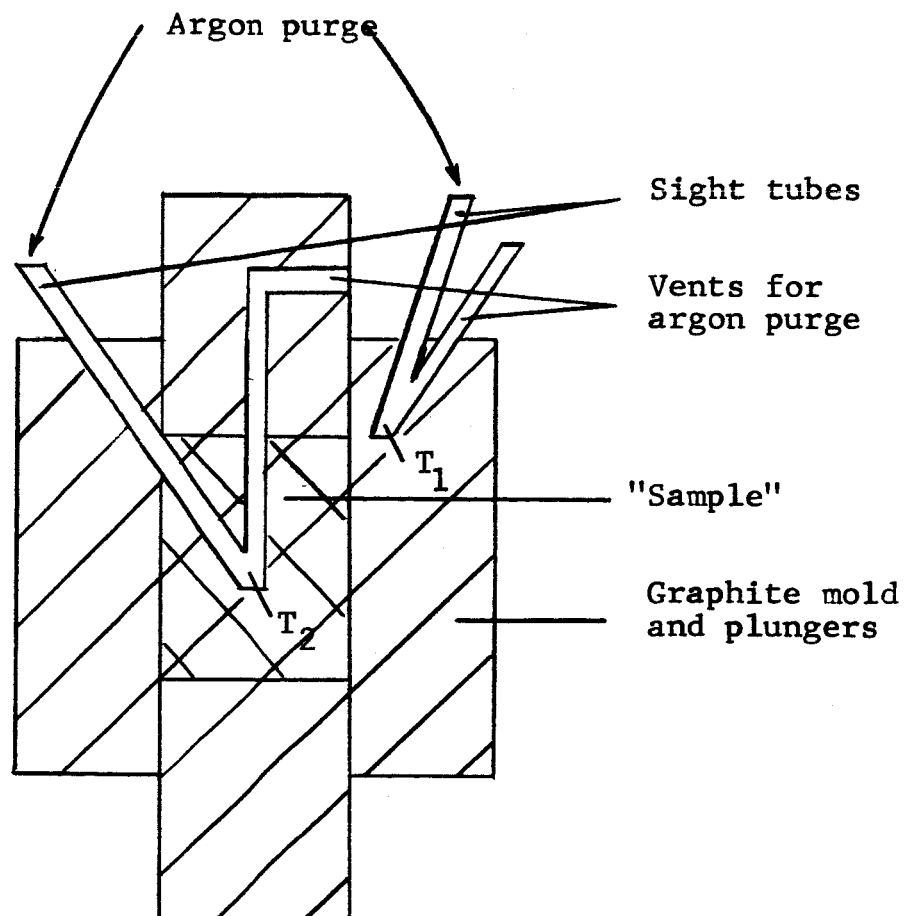


Fig 3 - DIAGRAM OF MOLD ASSEMBLY FOR
CALIBRATION BETWEEN SIGHT TUBE
AND SAMPLE TEMPERATURES

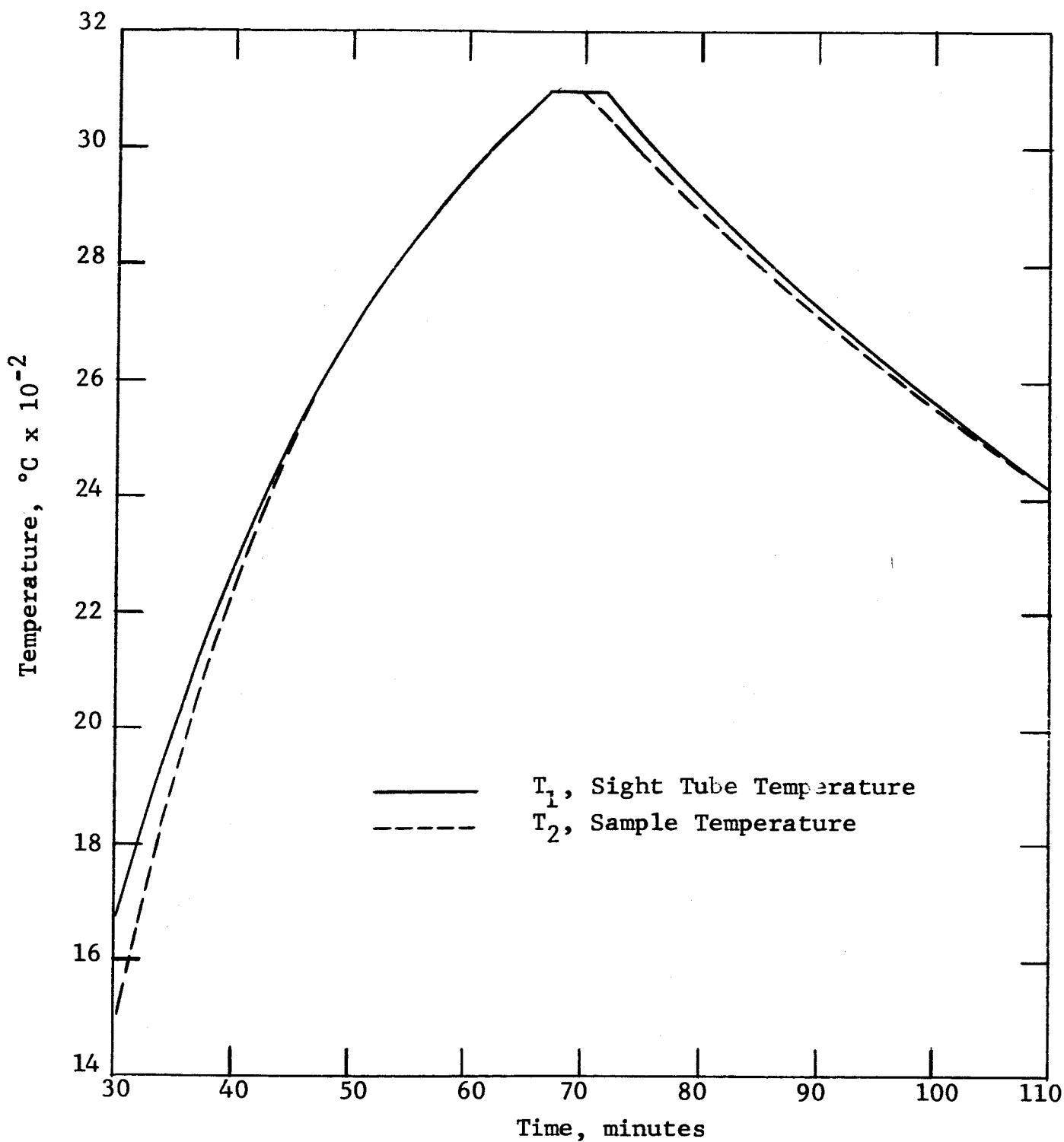


Fig 3a - SIGHT TUBE TEMPERATURE VS SAMPLE TEMPERATURE
DURING SIMULATED HOT PRESSING EXPERIMENT

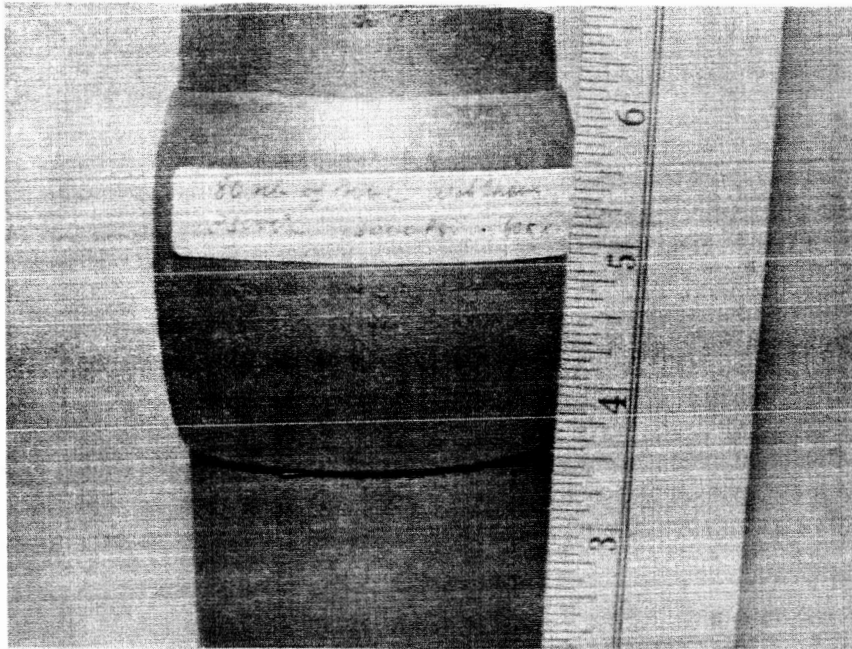
the system for the remainder of the heating cycle. During cooling, it would appear that the "sample" loses heat at a slightly more rapid rate than indicated through the sight tube.

3. Processing Procedure

During any particular hot pressing cycle, accurate estimation of ram movement necessary to attain maximum density was complicated by two factors: first, deformation occurred for all billets to varying extents depending on composition and processing parameters. Fig 4a shows a typical billet with attending deformation occurring during hot pressing. As can be seen, slight extrusion of the composition around the plunger is evident. The diameter of this particular sample ranged from 2.60 to 2.85 inches, whereas the diameter of the mold was 2.50 inches. Thus calculation of the finished theoretical height for maximum density was based on an estimated finished diameter of 2.8 inches.

The second factor which presented difficulties in accurate prediction of ram travel was significant changes in the graphite plunger lengths resulting from the compressive load at high temperatures. In Fig 4b, typical deformation of the plungers and mold is shown. Table I lists some typical deformations which occurred in various runs. Of course, part of the length change is attributable to diametral increases. In general, greater deformation was evident for the top as compared to the bottom plungers. The data to date is limited, however, and accurate prediction of plunger changes during hot pressing will require more information.

Reaction with the mold, which was a common occurrence for all compositions except tantalum carbide systems, can also be seen. Fig 5 is a microstructural study showing diffusion of carbide from a sample into the plunger.



(a)



(b)

Fig 4 - DEFORMATION OF SAMPLE, MOLD
AND PLUNGERS DURING HOT PRESSING

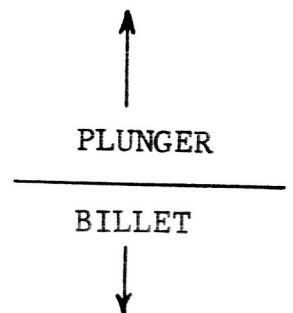


Fig 5 - MICROSTRUCTURE OF 70 wt% Nb COMPOSITE PRESSED
AT 3100°C SHOWING DIFFUSION OF NbC INTO PLUNGER
(320 X)

Table I
CHANGES IN PLUNGER LENGTHS
DURING HOT PRESSING

Composition wt% Metal	Temperature °C	% Change in Plungers		Actual Overall Change in Inches
		Top	Bottom	
50 Ti	2650	7.4	6.8	-1.56
50 Zr	2800	19.3	12.5	-3.50
80 Zr	2750	24.4	5.7	-3.31
50 Nb	3100	21.6	9.6	-3.43
60 Nb	3100	18.2	11.4	-3.26
70 Nb	3100	8.0	14.8	-2.51
82.5 Ta	3200	19.3	6.8	-2.84

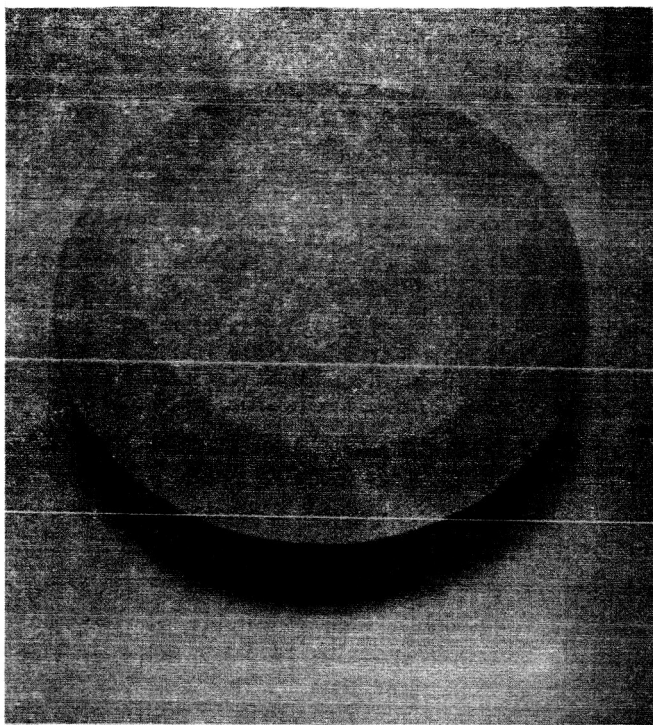
Thus the pressings were conducted by using ram movement values which included estimates (1/2 to 1 in.) to compensate for sample and plunger deformation. Attainment of maximum density was indicated by leveling off of the ram movement vs time curve based on estimated ram movement of 2 in. to 5 in. depending on system and composition.

4. Use of Higher Fabrication Pressures

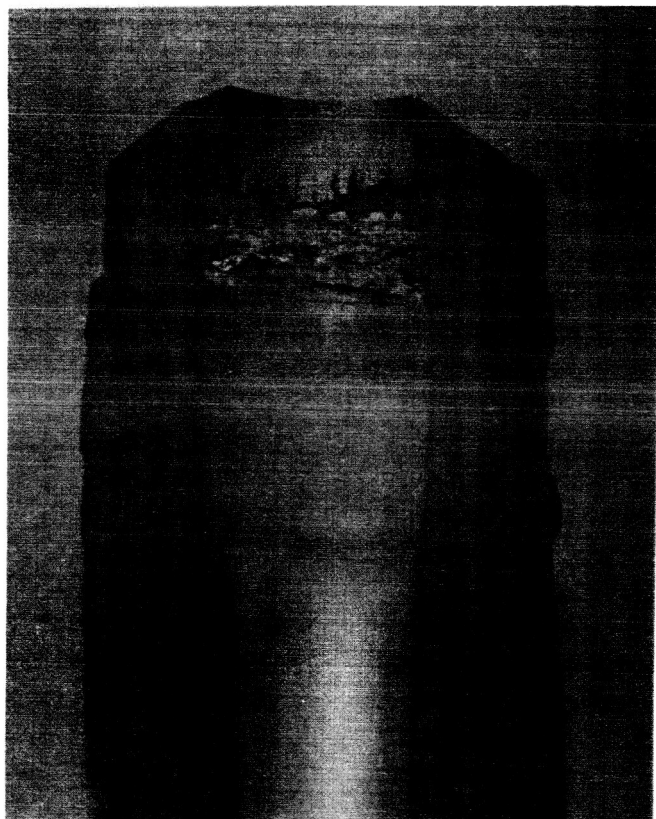
Most of the processings were conducted in Grade CS (Union Carbide) graphite molds. A limited series of tantalum and niobium compositions were fabricated in Grade ATJ molds so that higher (4000 vs 3000 psi) pressures could be attained with this stronger material. It was felt that higher pressures would increase sintering rates and enhance diffusion. The flexural and compressive strength² of these two materials are compared as follows:

	<u>CS</u>		<u>ATJ</u>	
	W/G	A/G	W/G	A/G
Flexural Strength, psi	2810	2400	4630	4000
Compressive Strength, psi	5990	5960	8330	8530

The experiments showed that there was no advantage in using the ATJ material. Although densification was somewhat accelerated by the use of the higher pressure, more extensive extrusion of material around the plungers not only caused loss of composition but also lead to misalignment of plungers and subsequent non-uniform pressing. A curious zoning occurred in the ATJ molds which was not seen in CS molds, (Figs 6a and 6b). There appears to be zones of reaction in the mold wall adjacent to the billet. Preliminary evaluation by metallographic examination and x-rays showed no presence of metal. Density and strength measurements will be conducted as further evaluation to determine if these affected areas differ from the parent ATJ stock.



(a) Horizontal Section of Top
of Mold Including Plunger



(b) Longitudinal Section of Mold
With Billet Removed

Fig 6 - ATJ MOLDS SHOWING REACTION ZONES
AFTER HOT PRESSING OF 70 wt% Nb COMPOSITES

5. Sample Preparation

To obtain the processed billet, the mold was cut open. Deformation of the sample configuration (increased diameter) occurring during pressing precluded simple ejection. Samples of both orientations for physical testing were sectioned and machined from halves of the finished billet which had a diameter of 2 1/2 inches and a height of approximately 2 inches, (Fig 7). Flexural test pieces measured 1/4 in. x 1/4 in. x 2 in. Compressive test specimens were 1/4 in. diameter x 3/4 in. high.

C. Measurement of Properties

Evaluation of finished composites included microstructural examination and determination of physical, mechanical, and electrical properties. The procedures used are described below:

1. Microstructural Examination

With the emergence of dense, hard structures in the present investigations, polishing difficulties such as "pullouts" which occurred with the much softer, porous bodies encountered in the previous work have been virtually eliminated. Samples for metallographic study were prepared using standard techniques of mounting in plastic, followed by grinding and polishing with silicon carbide and then with 9 μ diamond abrasive. Final polishing was accomplished on a silk cloth using slurry of ~0.05 μ alumina (Linde "B") in a 20% hydrogen peroxide solution. The H₂O₂ acted as a chemical polish-etch which minimized smearing and pullouts and also brightened the sample surface.

2. Physical Properties

Bulk density values were determined from precise measurements of dimensions and weight. The extent of densification was evaluated by comparison of these values to theoretical densities which was calculated simply as: (weight of metal carbide plus weight of graphite, all divided by volume of metal

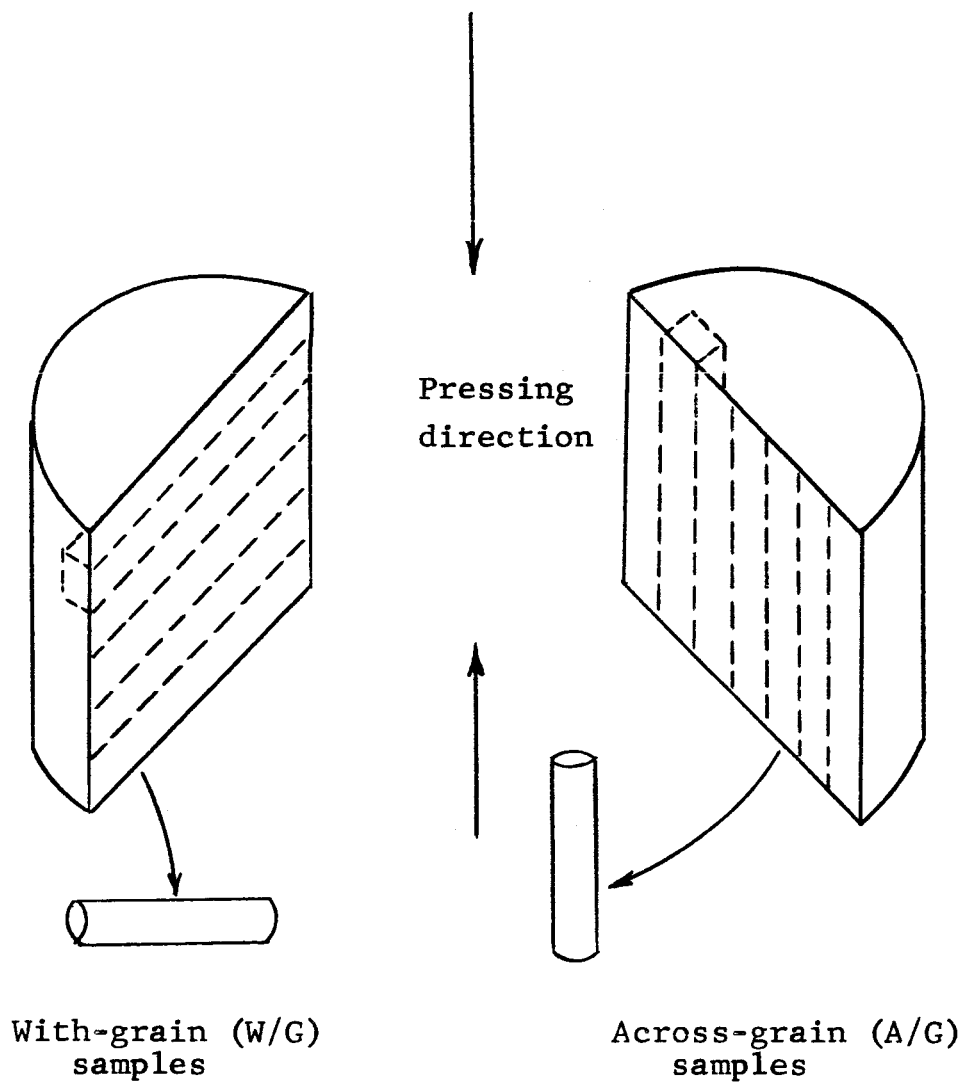


Fig 7 - SECTIONING OF BILLETS
FOR PROPERTY EVALUATIONS

carbide plus volume of graphite.) The calculations were made assuming the x-ray densities of the particular carbide and a value of 2.26 g/cc for the graphite phase. This is probably too high a figure since this would mean that the graphite was perfectly ordered, a condition approached only by pyrolytic material or single crystals. However for purposes of comparison in a single system or among different systems, these calculated theoretical densities form reasonable if not exact standards.

During the first year's program, density values as compared to calculated theoretical density quite often suggested gross porosity which was not corroborated by microstructural examination. Metal analysis conducted in the present investigation to determine actual metal content show that significant losses of metal had occurred in several of the pressings. Correction of theoretical density values to reflect actual rather than designated metal content has shown that most of the composites had attained densities of 90% or greater theoretical.

The procedure for determining metal content consists of oxidizing the metal carbide-graphite under a stream of oxygen at 900°C to obtain the metal oxide while volatilizing the carbon component as the monoxide and/or dioxide. Gravimetric analysis revealed the actual amounts of metal in the samples.

3. Mechanical Properties

Flexural strengths were determined using four point loading, the load points being at the 1/3 points of a 1 1/2 in. span. Room temperature measurements were conducted in a 5000 lb Riehle Testing machine. An extensometer was employed to record deflection of the sample; flexural modulus was determined from the x-y plot of stress vs strain. The elevated temperature evaluations were made in an argon atmosphere, using a graphite resistor tube furnace. Samples were heated to the respective test temperature in 5 to 15 min. and soaked for an additional

10 min prior to testing. Load was monitored with a calibrated deflection ring.

Compressive strengths were measured with a 10,000 lb Instron testing machine. Modulus determinations were made from x-y plots of deflection vs load. Compressive creep behavior was evaluated in the graphite resistor tube furnace in which sample deformation was monitored visually with a cathetometer. Heating rates were similar to those for flexural tests.

Each value in the physical property data represents an average of three or more determinations. Although the population of values is limited, the trends indicated by the data were deemed of greater importance than absolute data in this year's study. It was felt that the broad compositional studies would successfully suggest compositions which were worthy of more extensive study.

4. Electrical Properties

Electrical resistivity measurements were made on various samples to determine if any relationship existed between bonding and electrical properties. It was felt that extent of diffusion of the more conductive carbide or eutectic and hence, improved bonding would be detected by these experiments.

The electrical resistivity measurements were performed using a four-terminal method. Sample bars, 0.4 cm^2 cross section $(1/4 \text{ in.})^2$ and about 5 cm (2 in.) long, were used. Silver electrodes were applied at both ends and a constant current of 10 mA was passed through each sample by regulating the resistance in series with a battery. The potential drop in the direction of the current and near the center portion of the sample was measured several times, i.e., with a two contact voltage probe, (the distance between the contacts being 1 cm) and a Hewlett Packard 425A-type microvolt meter. Values for at least two of the four plane surfaces were averaged.

5. Thermal Shock Resistance

Preliminary experiments were conducted to examine resistance to thermal shock of various composites. The test consisted of rapid heating of one end of a 1/4 in. cross section test bar with a plasma jet at a 1/2 in. distance under an inert (argon) atmosphere. Three cycles of 30 sec on, followed by a cooling gas stream of argon, were used. The equipment used was a Plasmadyne SG-3, 25 KW unit mounted within a dry box arrangement, capable of a horizontal travel to obtain the on-off cycles on stationary samples.

III. RESULTS AND DISCUSSION

Investigations for this program have been concerned with metal levels of 50 wt% or greater in the various systems. Composites incorporating niobium carbide or tantalum carbide have received the most study since they displayed the best high temperature properties. The different systems and their properties are discussed individually in the following sections. Also presented are the results of experiments involving different carbon materials and studies of the relationship between processing temperature and carbide-carbon eutectic temperature.

The designation for composition has been by weight percent of metal for ease of reference. In addition, compositions are identified in terms of volume percent carbide, by which comparison of systems is simplified. For example, metal levels in a tantalum or a niobium system for a 50 volume percent carbide composite would be 82 wt% Ta or 69 wt% Nb. Fig 8 contains a plot of theoretical volume percent carbide as a function of weight percent metal.

A. Effect of Carbon Source

The following carbonaceous materials were examined

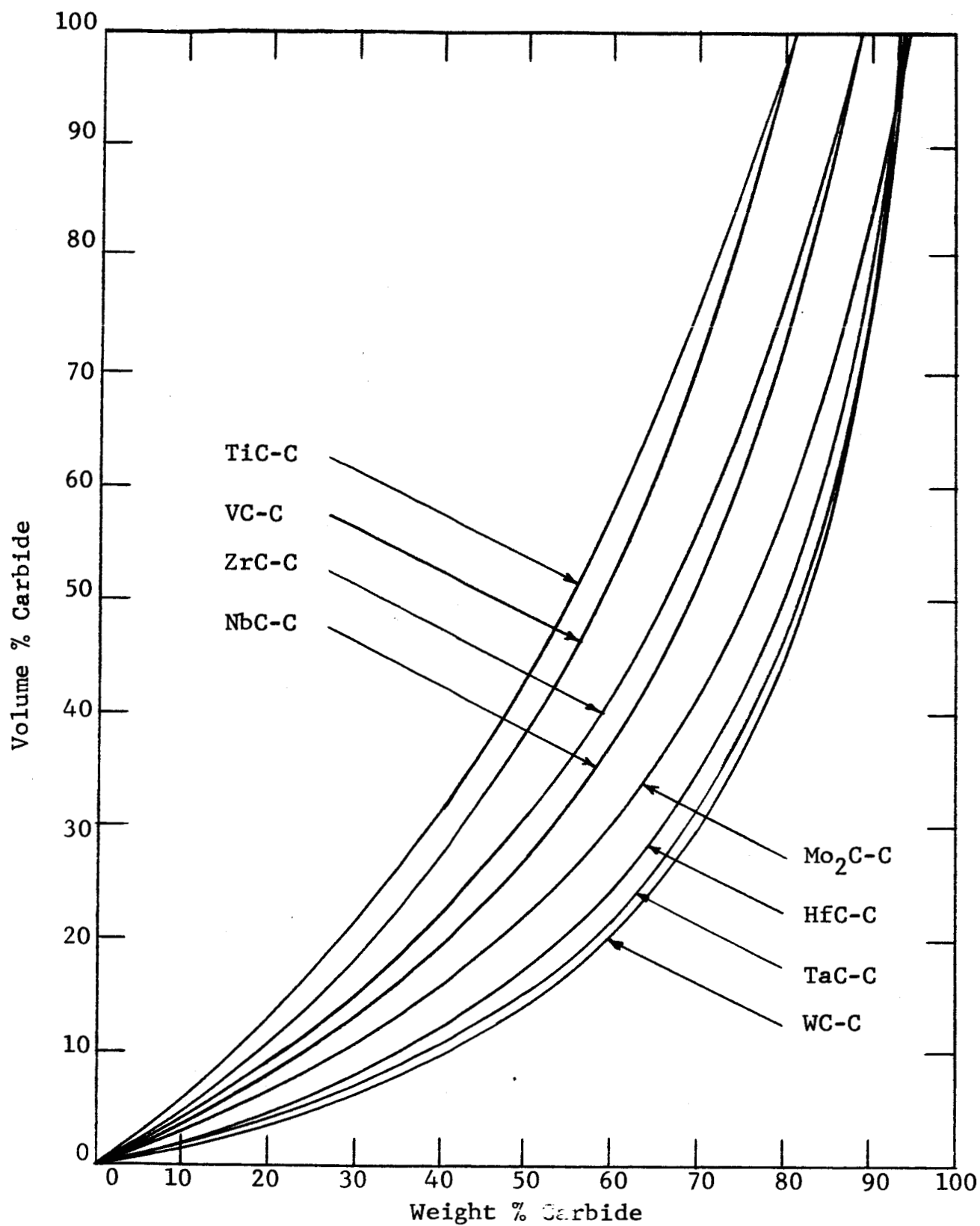


Fig 8 - THEORETICAL VOLUME % CARBIDE AS FUNCTION OF WEIGHT % METAL ADDITION

to determine the effect of type and shape of graphite source material on densification and bonding. The powders (all of less than 44μ particle size) which were examined are:

- a. Calcined petroleum coke (CPC) - has been the graphite source in past experiments. Particles are flat and plate-like and of high surface area.
- b. Calcined Gilsonite coke (GC) - particles are spherical.
- c. Synthetic resin coke (RC) - a highly cross linked structure with irregularly shaped particles.
- d. Synthetic graphite (BB) - an initial graphite structure material with particles of a shape similar to that for CPC.

These four carbons were hot pressed without additives at 3000°C under 3000 psi. Data in Table II show the densities and flexural strengths of the various bodies. Highest density was exhibited by CPC. The somewhat low density of RC can be attributed to limited graphitization and the true density of 1.52 g/cc for this material. Bonding was quite poor for all systems as seen by the flexural strengths of about 1000 psi. The GC samples in particular were quite fragile. Photomicrographs of the various systems are presented in Fig 9. Considerable porosity is seen to exist in all of the bodies.

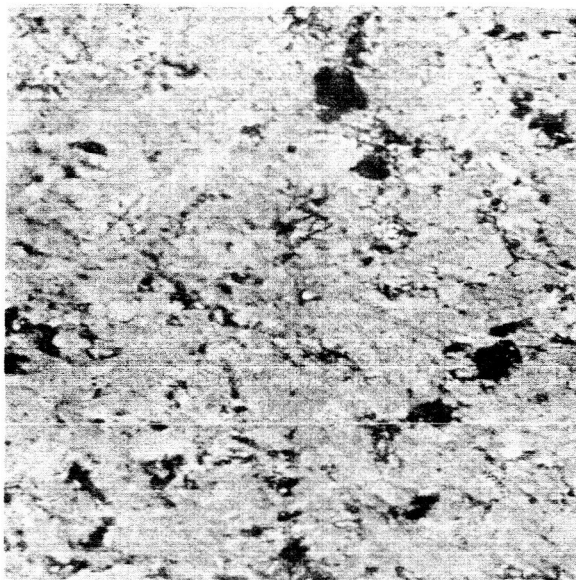
Examination by x-ray diffraction techniques revealed that CPC and BB were well graphitized and highly ordered. The GC sample showed a somewhat lesser degree of graphitization. The broadness of the diffraction pattern peaks and poor resolution indicated limited ordering in the RC. This is to be expected since RC is a "glassy" carbon with a high degree of cross linking which prevents easy graphitization.

Table II
EFFECT OF GRAPHITE SOURCE MATERIAL
ON DENSIFICATION AND BONDING

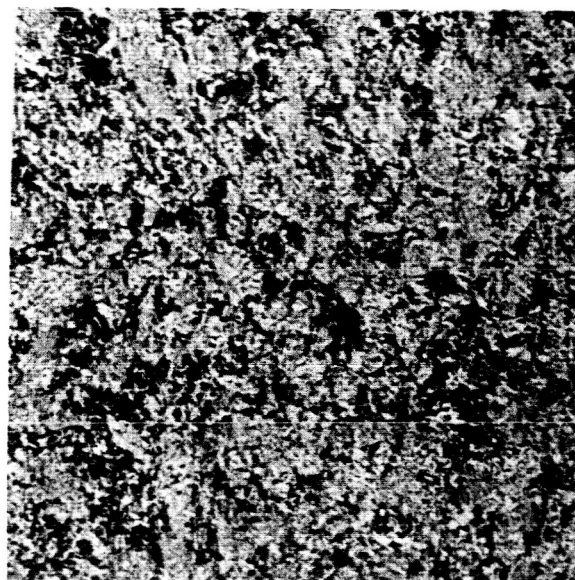
Carbon	No Additives		50 wt% Mo Addition			
	Density g/cc	Flexural Strength psi*	Density g/cc	Actual Metal Content wt%	Vol% Carbide	Flexural Strength psi
CPC	1.95	1420	2.88	34.1	13.4	13,130
GC	1.74	560	2.73	43.0	17.3	7,660
RC	1.41	1000	2.79	39.7	15.4	7,570
BB	1.78	1140	2.69	36.9	13.8	9,550

NOTE: All samples processed at 3000°C - 3000 psi

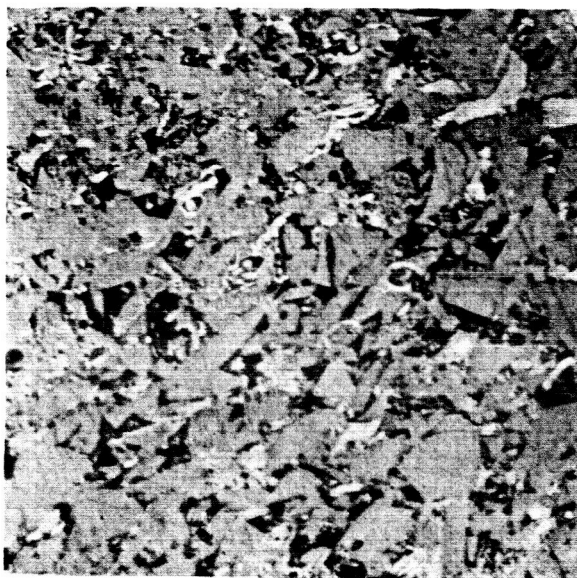
*In W/G direction



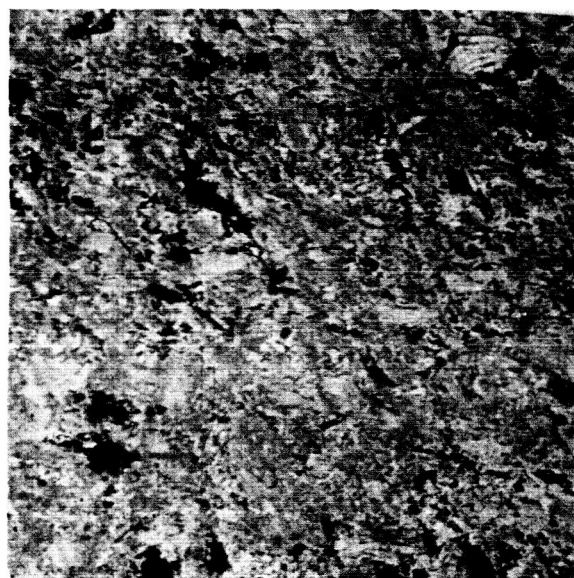
(a) CPC



(b) GC



(c) RC



(d) BB

Fig 9 - MICROSTRUCTURE OF HOT PRESSED GRAPHITE BODIES
USING DIFFERENT CARBON SOURCES (320 X)

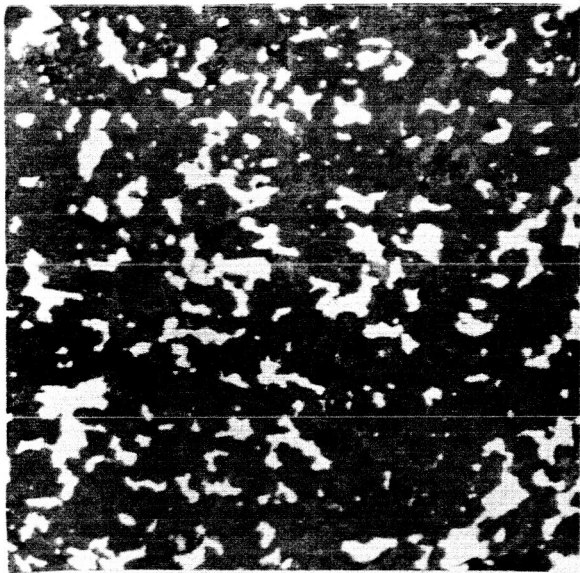
- (a) Calcined Petroleum Coke
- (b) Calcined Gilsonite Coke
- (c) Synthetic Resin Coke
- (d) Synthetic Graphite

Each of the four carbon sources were mixed with 50 wt% molybdenum and again processed at 3000°C. The strength data in Table II clearly shows the improved bonding attainable with the formation of the $\text{Mo}_2\text{C-C}$ eutectic ($\sim 2600^\circ\text{C}$) and subsequent recrystallization of the liquid phase. Highest strengths were exhibited by the CPC composition. The spherical cokes, i.e., GC and RC, achieved lower degree of bonding than "platy" CPC and BB.

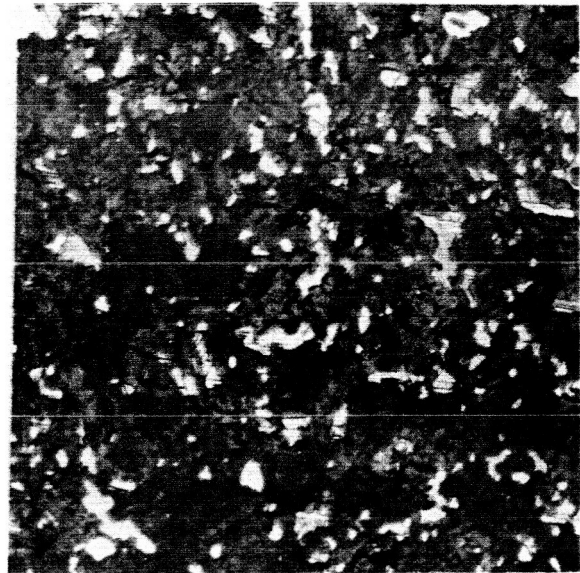
Metal analysis and calculation of percent theoretical density revealed that the lowest metal content among the finished billets was that of CPC-Mo which also showed highest densification. An inverse relationship exists between metal content and degree of densification. The CPC and BB systems appeared to have been "hot worked" to a greater extent resulting in greater loss of the molybdenum phase. This may be due to more rapid densification and subsequent squeezing out of the metal phase.

It is possible that with longer processing times, the compositions incorporating BB, RC or GC could be hot worked to the extent of the CPC body, resulting in greater metal loss and improved densification and bonding. The time available on the program did not permit extended investigation of such behavior. However, it is quite apparent that CPC composite exhibits the optimum properties under these processing conditions.

Microstructures of the four systems appear in Fig 10. It is interesting to note the relative size of molybdenum carbide particles. The finest structure and dispersion are in the RC and BB systems (Figs 10c and 10d) suggesting a more homogeneous distribution of the carbide-carbon eutectic phase. However, a relatively high degree of porosity exists in the RC system as seen in Fig 10c, and this probably is the reason for their lower strengths.



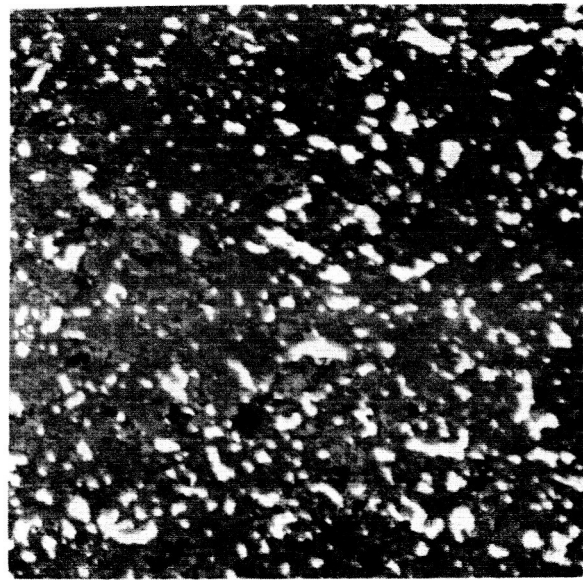
(a) 50 wt% Mo (CPC)



(b) 50 wt% Mo (GC)



(c) 50 wt% Mo (RC)



(d) 50 wt% Mo (BB)

Fig 10 - MICROSTRUCTURE OF 50 WT% Mo-GRAPHITE COMPOSITES
INCORPORATING DIFFERENT CARBON SOURCES (320 X)

- (a) Calcined Petroleum Coke
- (b) Calcined Gilsonite Coke
- (c) Synthetic Resin Coke
- (d) Synthetic Graphite

X-ray diffraction studies showed that all of the Mo containing systems were highly graphitized and ordered. With the addition of molybdenum, the resin coke system developed a well defined ordering. This can be due to either or both of the following mechanisms. First, the molybdenum in forming the carbide, would react with the more disordered carbon and permit easier graphitization of the less disordered material. Secondly, the formation of the carbide-carbon eutectic liquid would permit greater densification and ordering.

The experiments revealed that plate-like carbon particles are preferable for attaining good densification and bonding in hot pressed metal-graphite composites. Calcined petroleum coke is a good choice in this respect. Liquid phase sintering is clearly available with the addition of molybdenum, and graphitization of any carbon material would appear feasible through such metal addition.

B. Niobium Carbide-Graphite System

The potential exhibited in the earlier work of the niobium system (16,000 psi room temperature flexural strength)¹ had made it a prime candidate for additional study in this program. The present investigations of this system have involved metal contents up to 85 wt% niobium (greater than 88 volume percent carbide). Some of the higher metal content composition formed a very weak eutectic structure. These received only metallographic examination; only billets which could be sectioned into test specimens are included in Table III. Property evaluations were curtailed for any composition when it became obvious that the particular composite did not represent a material with optimum structural characteristics.

Microstructural Studies - Initial pressings for the niobium system were conducted at 3000°C. As seen by the data for 50 Nb, 65 Nb and 65 Nb-A, strengths were disappointingly low (6000 -

Table III
SUMMARY OF NbC-C SYSTEM: FABRICATION DATA

Compositional Designation	Form of Metal Addition	Pressing Temp °C	Wt% Metal		Volume % Carbide	Density g/cc	%Theor. Density
			As Mixed	Actual			
50 Nb	Metal	3000	50	50.4	27.5	3.51	92.6
50 Nb-31	Metal	3100	50	48.2	25.6	3.42	92.7
50 Nb-A*	Metal	3200	50	(a) 22.6 (b) 40.2	(a) 9.0 (b) 19.4	(a) 2.56 (b) 3.05	(a) 92.8 (b) 91.3
65 Nb	Metal	3000	65	--	44.2	4.44	93.8
65 Nb-A	Metal	3000	65	--	44.2	4.45	93.9
70 Nb	Metal	3100	70	70.8	53.6	5.03	97.3
C-70 Nb	Carbide	3100	70	70.0	52.2	4.95	95.7
80 Nb-S	Metal	3000	80	--	72.9	6.10	96.4
80 Nb-A	Metal	3200	80	80.6	74.5	6.03	94.2
80 Nb-B	Metal	3000	80	--	72.9	6.16	97.3
C3-80 Nb	Carbide	3000	80	79.8	72.5	6.08	97.6
81.3 Nb	Metal	3000	81.3	81.3	76.4	6.30	96.5
84 Nb	Metal	3000	84	--	84.2	6.61	94.8
85 Nb	Metal	3000	85	85.3	88.4	7.04	98.0

*Heterogeneous body. Upper portion of billet presented as (a) and lower portion as (b)

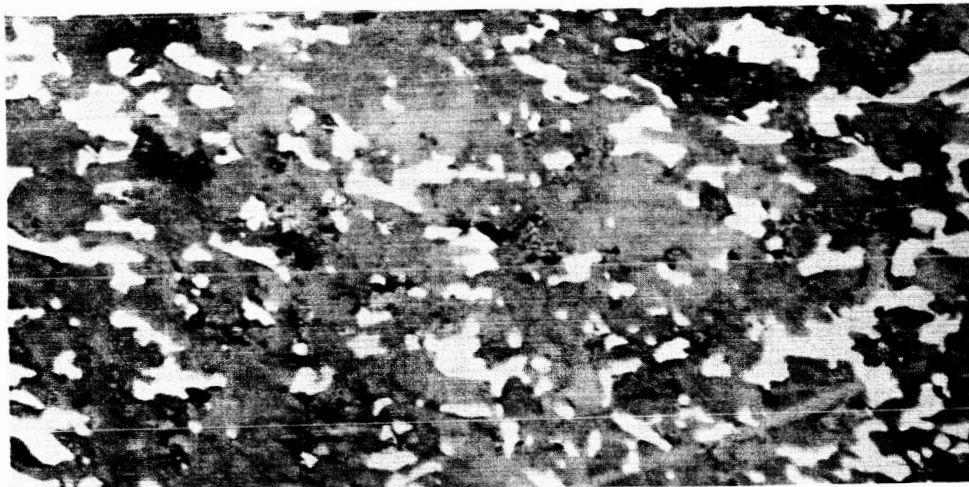
Table IIIa
SUMMARY OF NbC-C SYSTEM: PROPERTIES DATA

Compositional Designation	Flexural Strength, psi			Flexural Modulus x 10 ⁶ psi	Compressive Strength psi	Compressive Modulus x 10 ⁶ psi	Grain Direction
	Room Temp	2000°C	2500°C				
50 Nb	6,100	9,100	--	--	--	--	W/G
50 Nb-31	14,530	21,080	19,450	2.54	9,200	1.86	W/G
50 Nb-A	11,450	--	12,090	2.99	--	--	W/G
65 Nb	8,070	10,800	--	--	--	--	W/G
65 Nb-A	8,380	12,810	--	--	--	--	W/G
70 Nb	17,050	18,160	12,560	5.23	29,300	4.68	W/G
C-70 Nb	7,410	9,370	7,700	2.75	--	--	A/G
	20,160	--	12,220	10.53	27,600	3.78	W/G
80 Nb-S	19,130	21,700	16,320	24.00	52,940	9.76	W/G
80 Nb-A	16,790	17,310	creep	21.03	--	--	W/G
	10,370	11,050	creep	13.94	--	--	A/G
80 Nb-B	--	25,290	16,470	--	--	--	W/G
C3-80 Nb	6,660	--	--	4.16	32,700	2.68	W/G
	4,010	--	--	3.70	--	--	A/G
81.3 Nb	24,190	25,270	--	25.60	75,750	9.40	W/G
84 Nb	23,200	>24,700	--	29.52	115,480	32.16	W/G
85 Nb	26,040	>30,000	23,000	15.86	187,000	11.16	W/G

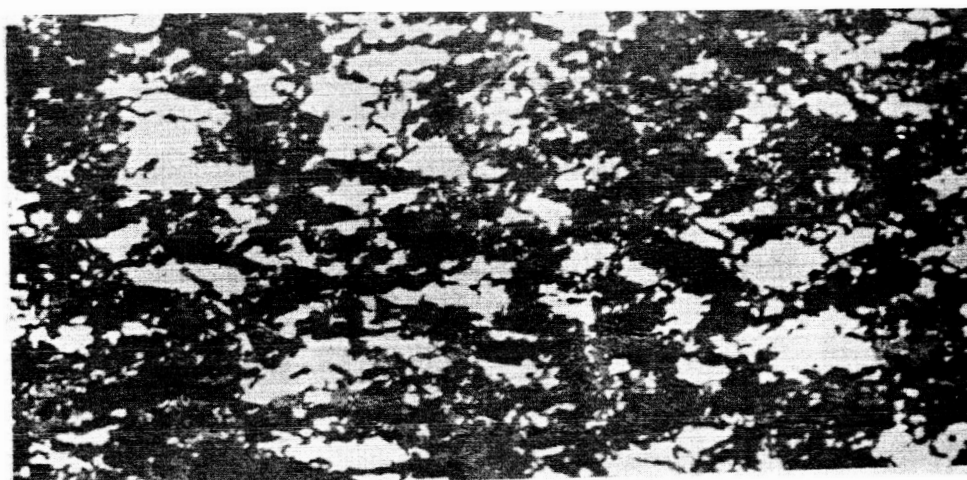
8000 psi), although high densities were achieved. The microstructure shown in Fig 11d reveals large, oriented carbide particles. In contrast, a completely different structure was exhibited by the 16,000 psi, 50 wt% sample fabricated during the first year's program. This particular sample had an actual metal content of 42.4 weight percent and as Fig 11c shows, the particles were much smaller and their shape suggests melting and recrystallization. It is probable that this high strength composite was obtained by exceeding the nominal temperature of 3000°C to a closer approach to the NbC-C eutectic temperature of 3250°C³; the higher temperatures would aid in diffusion and the presence of a liquid phase would enhance sintering.

Compositions of 50 wt% Nb pressed at higher temperatures exhibited improved bonding. At a 3100°C processing temperature, high strength composites were produced (see 50 Nb-31 in Table III). Fig 11b reveals some fairly large carbide grains; distribution appears fairly uniform. Hot pressing of 50 wt% Nb at 3200°C resulted in substantial losses of the metal phase as seen by the data for 50 Nb-A. Interestingly, samples containing smaller amounts of metal (about 25 wt%) showed strengths less than 10% lower than those having about 40 wt% metal. The microstructure (Fig 11a) indicates some melting and recrystallization of the carbide phase.

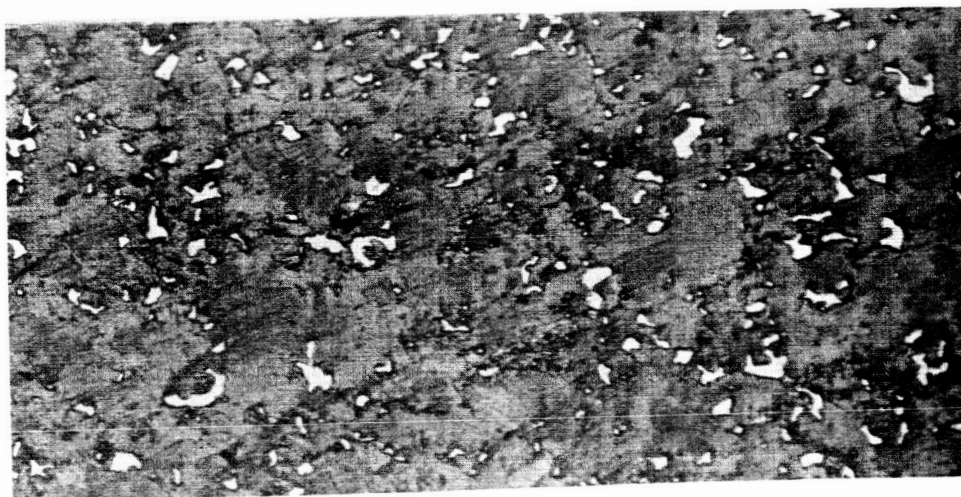
At the 70 wt% level, NbC constitutes about one half the volume of the composite. Strength data (17,000 - 20,000 psi) showed these composites to be well bonded. As described earlier, NbC as obtained from the supplier was significantly finer in particle size than the metal. Figs 11e and 11f reflect this difference in the hot pressed composites. With the higher metal content compositions of 80 wt% Nb, it was evident that the eutectic temperature of 3250°C had been exceeded with some of the pressings. Two such billets are shown in Fig 12. Zones



(a) 50 wt% Nb
Pressed at
3200°C
(50 Nb-A)*



(b) 50 wt% Nb
Pressed at
3100°C
(50 Nb-31)*



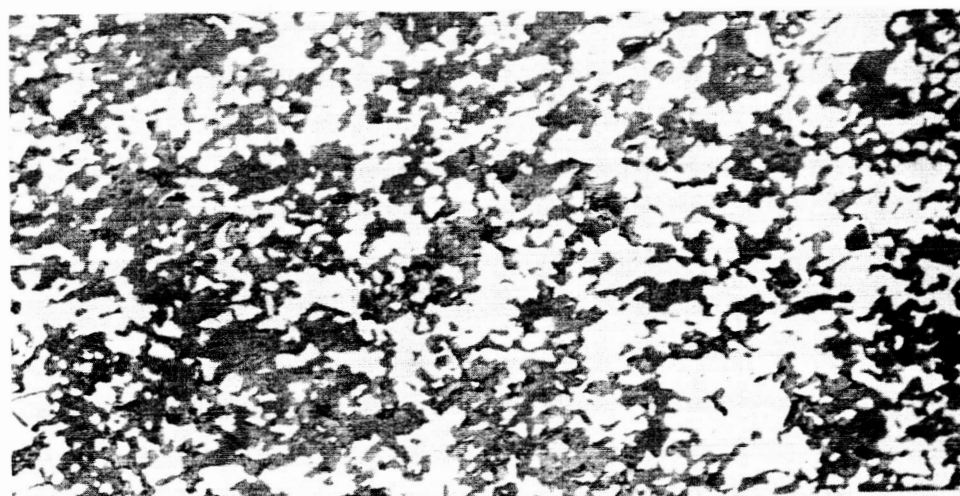
(c) 50 wt% Nb
Pressed at
"3000°C"
(Reference 1)

* See Table V

Fig 11 - MICROSTRUCTURE OF NbC-C COMPOSITES (320 X)



(d) 65 wt% Nb
Pressed at
3000°C
(65 Nb-A)*



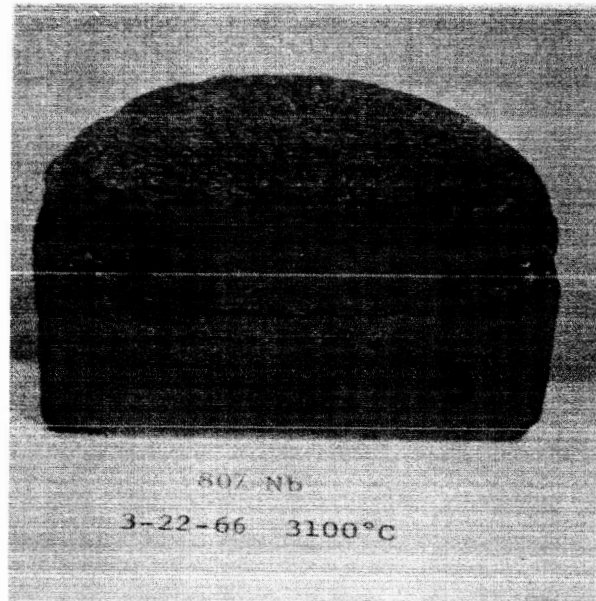
(e) 70 wt% Nb
Pressed at
3100°C Using
NbC
(C-70 Nb)*



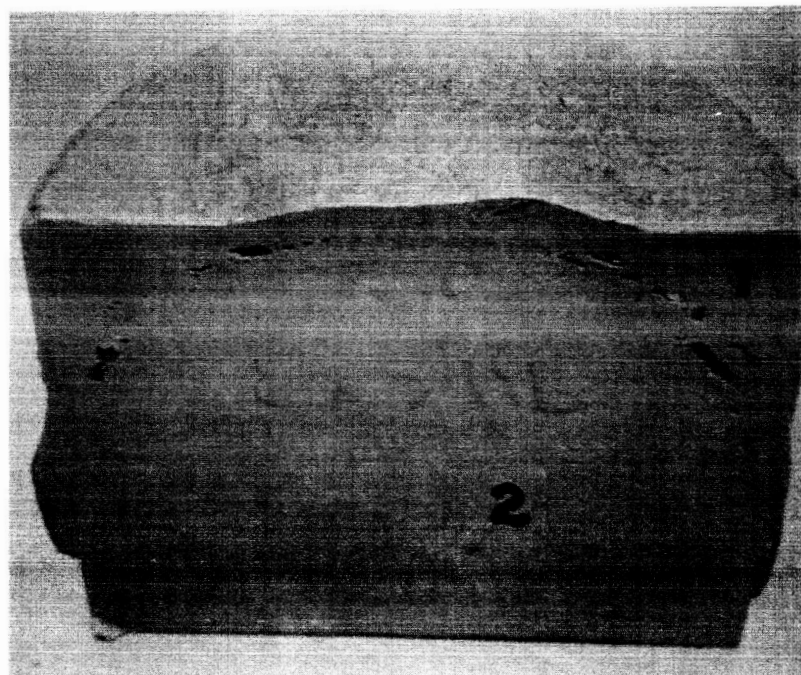
(f) 70 wt% Nb
Pressed at
3100°C Using
Nb Metal
(70 Nb)*

* See Table V

Fig 11 - MICROSTRUCTURE OF NbC-C COMPOSITES (320 X)



(a)



(b)

Fig 12 - BILLETS OF 80 WT% Nb COMPOSITES
PRESSED AT 3000 PSI AND 3200°C

within the billets have been designated (1), (2) and (3) in Fig 12a and (1) and (2) in 12b. Sample (a) showed distinct zones of graphite (1), large recrystallized melt (2), and what appeared to be a dense, homogeneous area (3). Not included in this photograph are additional zones of recrystallized melt above zone (1) which fell away from the rest of the sample in removal from the mold.

Zone (2) was extremely fragile and contained shiny platelets of graphite which had apparently exsolved. Photomicrographs (Fig 13) reveal a eutectic structure with long platelets of graphite similar to that found in arc-cast TiC-C and ZrC-C of hypereutectic composition.⁴ The 80 wt% Nb composition is also a hypereutectic, the eutectic being 81.3 wt% Nb. Fig 14 shows the structure in zone (3). Again, a eutectic structure is revealed with larger amounts of graphite. A much more finely structured eutectic is seen in the center.

As seen in Fig 12, zoning occurring in sample (b) appeared to follow lines of pressure, i.e. zone (1) above the conical zone (2) was probably under the highest compressive forces during hot pressing. Microstructural study revealed a eutectic structure in zone (1) but not in zone (2) - Fig 15. Thus the more intimate contact between the carbide and graphite phases in zone (1) was probably responsible for the resulting two types of structure within this billet.

It is evident from these samples that formation of eutectic in high metal content compositions produces bodies having serious flaws. Such high temperatures may not be deleterious if a lower metal content such as 50 wt% is used since melting would be in isolated islands. However, in an 80 wt% mixture which is quite close to the eutectic (81.3 wt%) composition, practically the whole sample melts, resulting in gross loss of material thru extrusion around the plungers and reaction with the mold. Heterogeneity also can result due to different rates

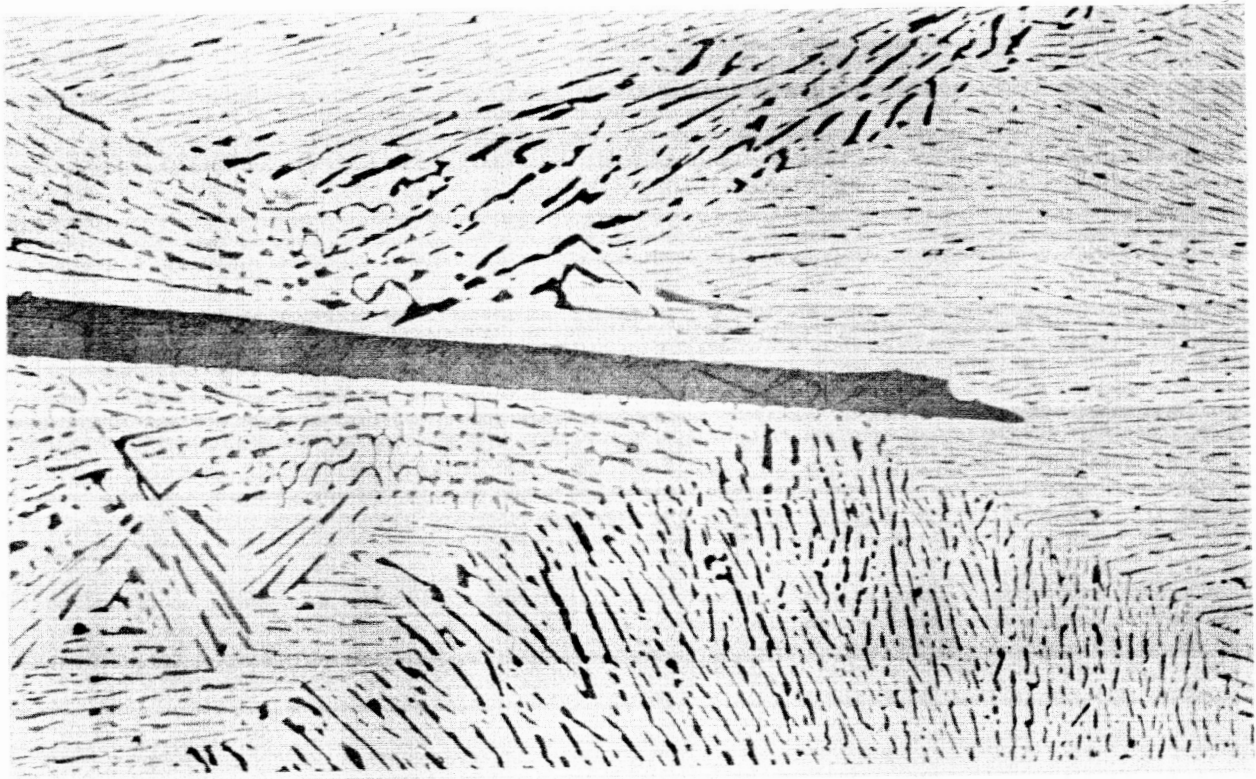
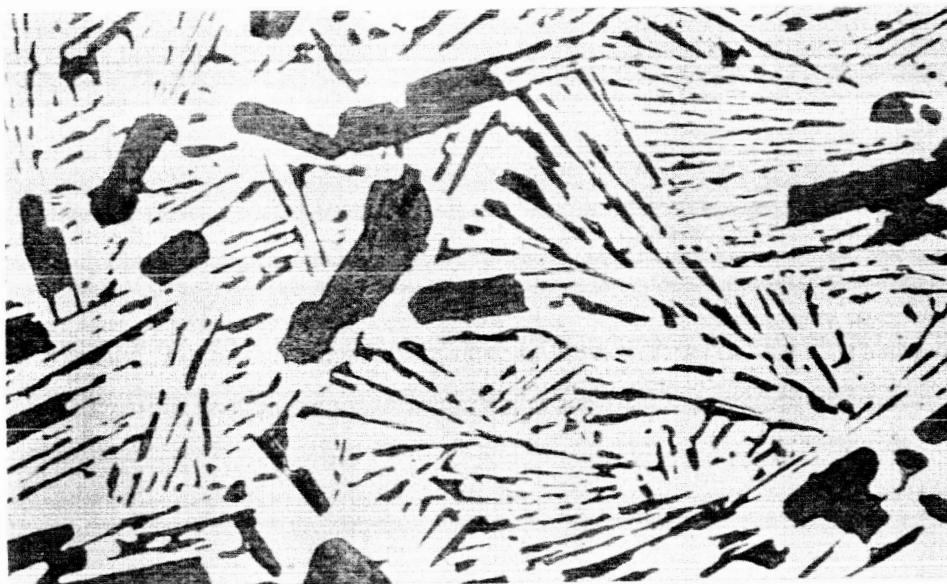


Fig 13 - MICROSTRUCTURE OF ZONE (2) IN 80 WT%
COMPOSITE (SAMPLE a) SHOWING EUTECTIC
STRUCTURE (200 X)



Fig 14 - MICROSTRUCTURE OF ZONE (3) IN 80 WT%
Nb COMPOSITE (SAMPLE a - 200 X)



(a) Zone 1



(b) Zone 2

Fig 15 - MICROSTRUCTURE OF 80 WT% Nb
COMPOSITE (SAMPLE b - 320 X)

of crystallization.

An example of the extent of melting which occurs for a low metal content body vs that for a eutectic composition is illustrated in Fig 16 for zirconium bodies heat treated at approximately 2800°C. Both samples were of a bar shape prior to heating. The bar structure is still discernible for the 50 wt% sample on which beads of recrystallized melt can be seen; however, collapse of the shape is evident for the 80.7 wt% specimen.

Processing of the ≥ 80 wt% Nb compositions at 3000° - 3100°C yielded structures in which the eutectic and attending flaws were absent. The major constituent at these metal levels is the carbide phase. Figs 17a through 17e reveal this dominance and also good continuity in the carbide phase. These photographs represent the desirable structures for hot pressed composites in contrast to the eutectic. At the 85 wt% metal level, the carbide occupies 88% of the total volume (Fig 17e) whereas an 80 wt% composition corresponds to about 73 vol% (Fig 17a). The significance of reference to volume % carbide as well as wt% metal is shown by this comparison.

X-ray powder patterns were obtained for the various compositions. These studies revealed NbC (monocarbide) and graphite. There was no evidence of NbC_{1-x} , Nb_2C or free metal.

Mechanical Properties - The property of composites which has received the most study has been flexural strength. This has been predicated on the ease of fabricating a sample specimen shape and on the speed and simplicity of flexural evaluations. A good screening of high temperature behavior of potential systems is accomplished.

During testing at temperatures of 2500°C or higher, creep behavior was exhibited by all samples to varying degrees.

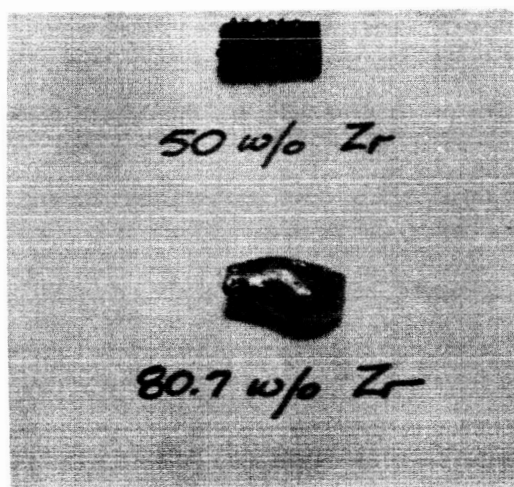
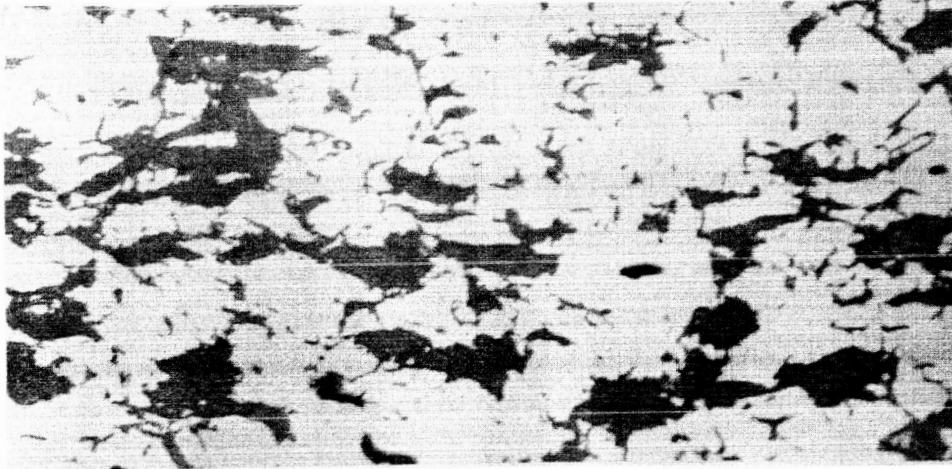
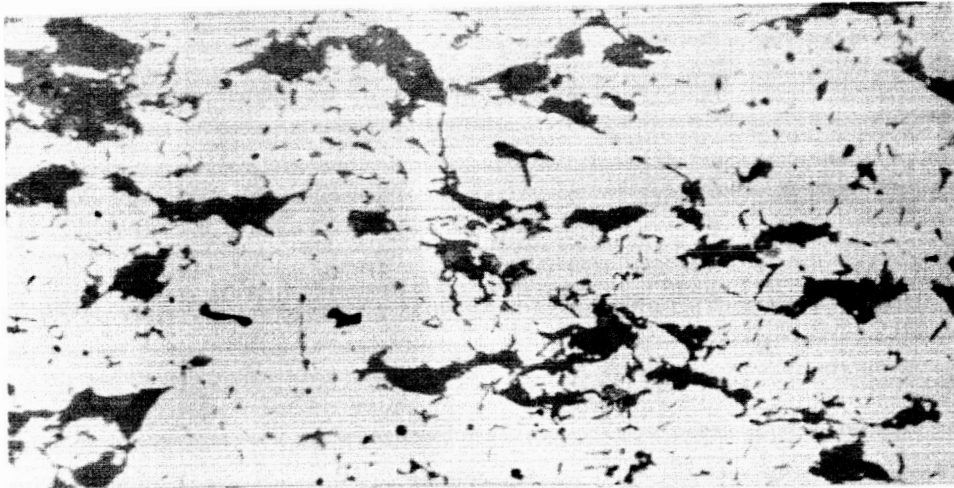


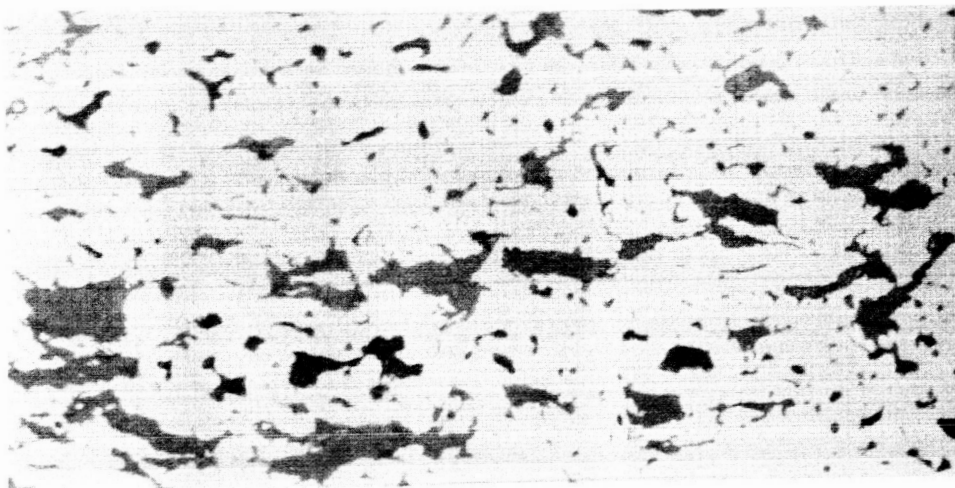
Fig 16 - ZIRCONIUM CARBIDE - GRAPHITE SPECIMENS
HEAT TREATED AT 2800°C/10 MINUTES



(a) 80 wt% Nb
Pressed at
3000°C
(80 Nb-S)*



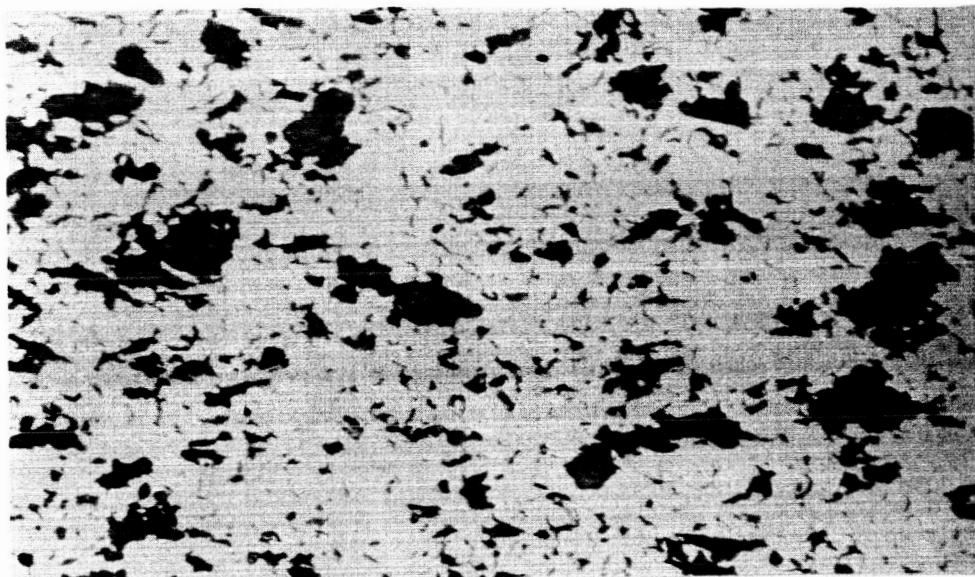
(b) 81.3 wt% Nb
Pressed at
3000°C
(81.3 Nb)*



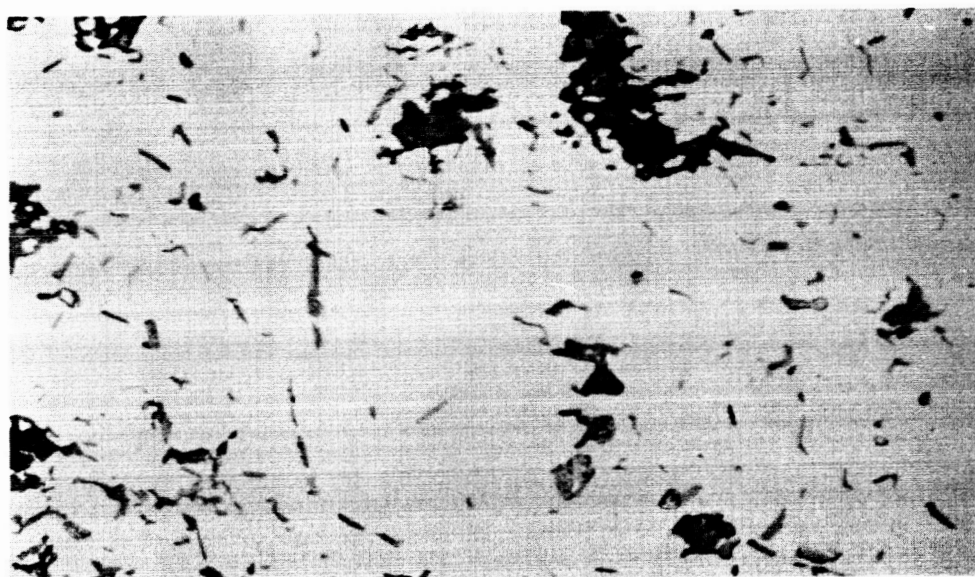
(c) 84 wt% Nb
Pressed at
3000°C
(84 Nb)*

* See Table V

Fig 17 - MICROSTRUCTURE OF HIGH METAL
CONTENT NbC-C COMPOSITES (320 X)



(d) 80 wt% Nb
Pressed at
3000°C Using
NbC
(C3-80 Nb)*



(e) 85 wt% Nb
Pressed at
3000°C
(85 Nb)*

* See Table V

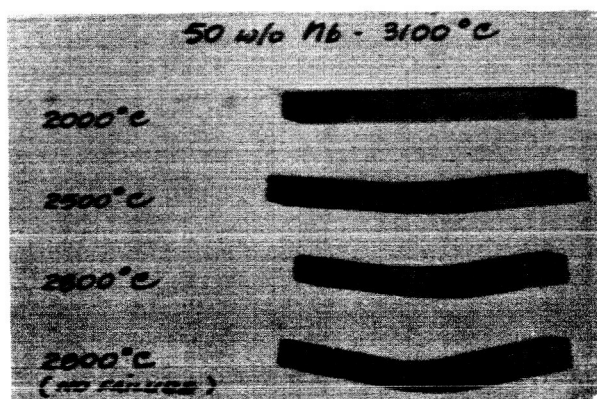
Fig 17 - MICROSTRUCTURE OF HIGH METAL
CONTENT NbC-C COMPOSITES (320 X)

Specimens which deformed considerably could not be stressed to failure since deflection was limited to a 1/8 in. vertical travel; at this point, the sample made contact with the graphite boat which supports the sample.

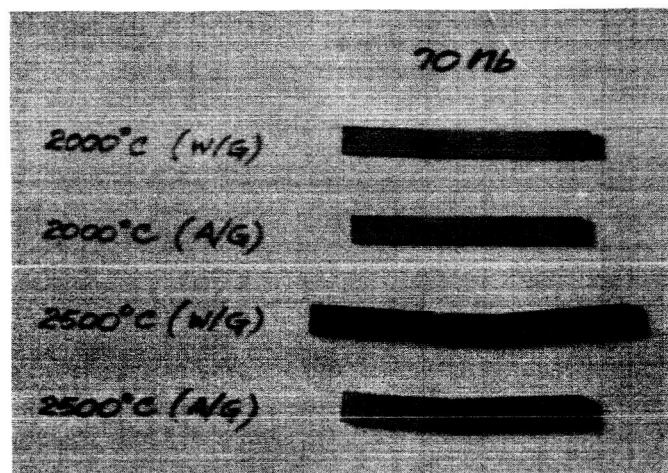
Excellent retention of strength at high temperatures was exhibited by 50 Nb-31 (Table III). At 2500°C, the flexural strength was substantially higher than at room temperature. At a test temperature of 2800°C, failure occurred at about 14,000 psi for some samples while others of the same composition were stressed to a load of 25,000 psi without failure. The extent of deformation which occurred at the test temperatures is illustrated in Fig 18a.

Increased strength at higher temperatures peaking at about 2000°C was observed for all NbC-C compositions. Flexural strengths as a function of temperature for NbC-C composites is illustrated in Fig 19. This behavior is similar to that for graphite which attains a maximum at about 2500°C. In contrast carbides generally display an inverse relationship between strength and temperature.⁵ A possible explanation is that at room temperature, residual forces prevail in the carbide and/or graphite phase, brought on by difference in thermal expansion when cooling occurs from fabrication temperature. These detrimental forces tend to disappear as the material is heated so that at 2000°C, a body which is relatively stress free exists.

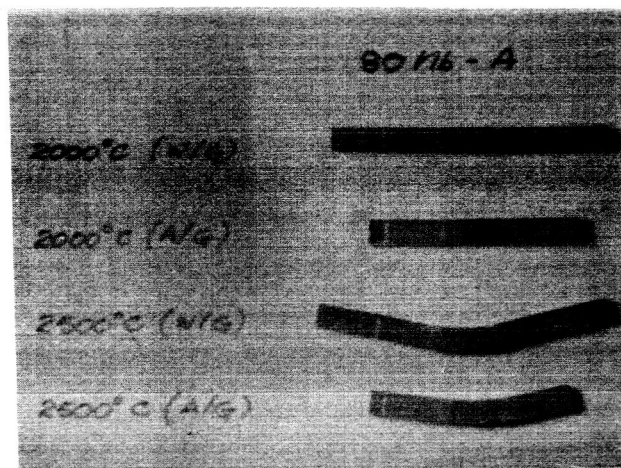
A comparison of density between well bonded 50 Nb-31 (3.42 g/cc) and poorly bonded 50 Nb (3.51 g/cc) indicates that degree of densification is not the main factor. Metal analysis has shown that the strong 3.42 g/cc material had an actual metal content of 48.2% and had attained 92.7% theoretical density; the weaker 3.51 g/cc material contained 50.4 wt% metal and was 92.6% theoretical density. From the similarity in metal content and degree of densification, it would appear that



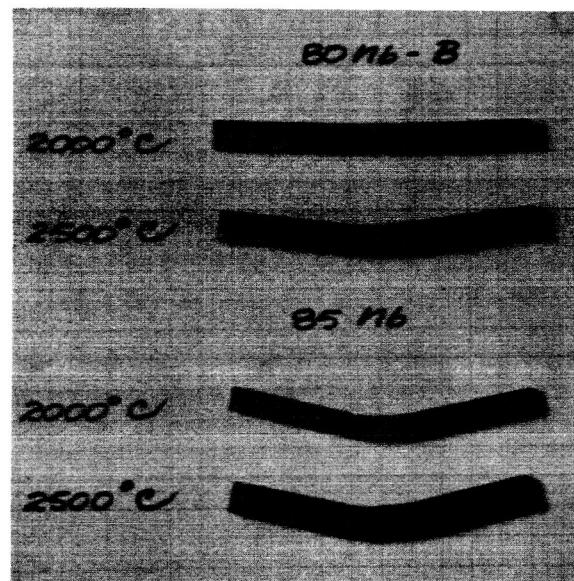
(a)



(b)



(c)



(d)

Fig 18 - HIGH TEMPERATURE FLEXURAL TEST SAMPLES
OF NbC-C COMPOSITIONS

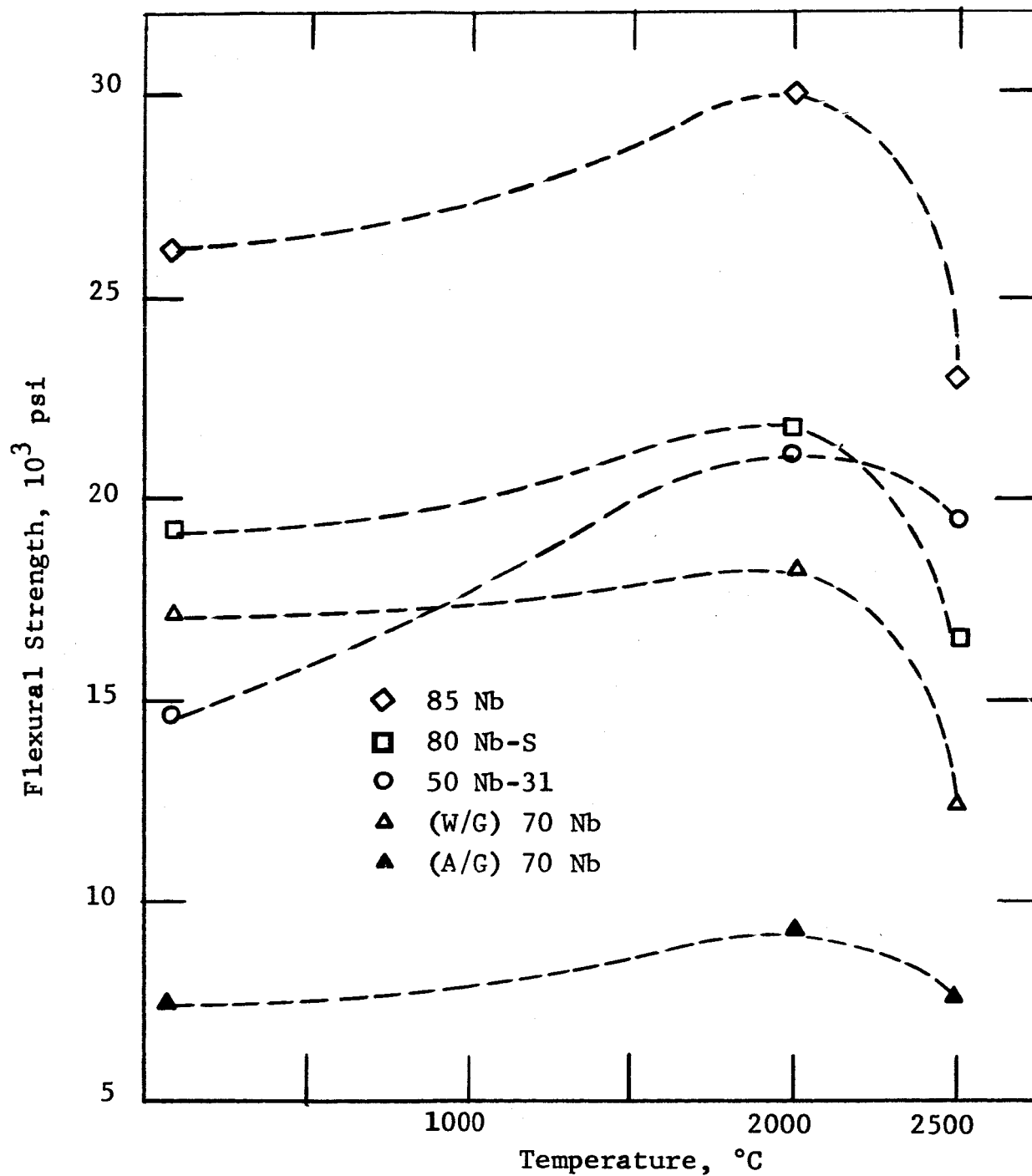


Fig 19 - HIGH TEMPERATURE FLEXURAL STRENGTH
OF NbC-C COMPOSITES

the higher processing temperature was more conducive to NbC-C eutectic diffusion and also to a higher degree of graphitization, thus yielding stronger bonds. The effect of enhanced diffusion on the strengths of hot pressed NiO bodies of equal density has been reported.⁶

Composites containing 70 wt% Nb displayed a slight increase in strength at 2000°C and a fairly strong dropoff at 2500°C. As illustrated in Fig 18b, the plastic deformation which occurred during testing was similar to that for 50 wt% Nb. The anisotropy ratio was 2.3 at room temperature, whereas for 50 wt% Nb, the ratio was closer to 4. Thus the presence of greater amounts of the cubic carbide appears to lessen directionality in properties. Furthermore, the ratio for 70 Nb drops to 1.9 and 1.6 respectively at 2000°C and 2500°C. This trend toward isotropy is due mainly to a greater increase in strength at the higher temperature in the A/G direction. The reason for this behavior is not understood at this time. However, the superior maintenance of strength in the weaker A/G direction as compared to the W/G direction at higher temperatures can be a desirable property; such non-directionality may allow for easier design of components.

At the higher metal levels of 80 wt% and 70 vol% carbide, room temperature flexural strengths were generally higher than those of lower metal content. Thus within the range of compositions studied, strength increases with metal content. However, one high metal composite which was obviously poorly bonded was C3-80 Nb which exhibited strength of only 6600 psi (W/G) and 4010 psi (A/G). As the microstructural study (Fig 17d) showed the carbide phase did not appear as continuous and well sintered as in the other 80 wt% Nb composites. It would appear that longer times at temperature and/or higher temperature (but still below the eutectic) are necessary in hot pressing of this particular composition to obtain optimum properties.

The 80 - 85 wt% Nb composites all showed significantly lower strengths at the higher temperatures as compared to room temperature values. Furthermore as illustrated in Fig 18, samples tested at 2500°C deformed considerably as compared to corresponding 50 and 70 wt% composites. The 85 wt% Nb samples tested at 2000°C also exhibited plastic deformation whereas little if any was seen for lower metal content samples tested at this temperature. It appears from these experiments that high temperature plasticity is a direct function of metal content. This appears logical in that the creep behavior of NbC is reported as severe at 2190°C.⁵ Therefore, when the carbide becomes the matrix material in the composite, the carbide properties begin to dominate. Of course plasticity is also a function of loads applied, and it is possible that at lower pressures plastic deformation would not occur in the various NbC-C composites.

Elastic modulus in flexure and compressive strength also are a direct function of metal content. In compositions where graphite is the matrix (50 wt% Nb) these properties were similar in magnitude to those of premium grade graphites such as ATJ. With compositions having greater than 50 vol% carbide, these values increase sharply. As reported in Table III compressive strengths of greater than 100,000 psi exist for compositions in the hypoeutectic region.

For a material to be useful at high temperatures, its resistance to creep or plastic deformation is of primary importance. Unless a system can maintain its structural integrity under load, its utility would be severely limited. For this reason, compressive creep experiments were made to compare results with observations from the flexure tests. Compressive deformation experiments were conducted on various compositions which were tested in the form of 1/4 in. diameter x 3/4 in. high right cylinders. The data are tabulated in Table IV.

Table IV
HIGH TEMPERATURE COMPRESSIVE DEFORMATION
OF NbC-C COMPOSITES

Compositional Designation	Composition Wt% - Metal	Pressing Temp °C	Grain Dir.	Test Conditions			$\frac{\Delta L}{L_0}, \%$	$\frac{\Delta D}{D_0}, \%$
				Temp, °C	Load, psi	Time, min		
50 Nb-31	48.2-Nb	3100	W/G	2500	4000	60	-6.2	--
50 Nb-31	48.2-Nb	3100	W/G	2650	2000	30	-0.4	+2.4
70 Nb	70.8-Nb	3100	W/G	2600	2000	30	-1.3	+1.5
80 Nb-S	80-Nb	3000	W/G	2550	2000	30	-1.6	+1.2
84 Nb	84-Nb	3000	W/G	2500	2000	30	-1.2	+1.3
85 Nb	85.3-Nb	3000	W/G	2600	2000	30	-0.3	-0.3

Due to some experimental difficulties, the desired test temperature of 2700°C was not attained. However, at the levels of 2500° - 2650°C with a load of 2000 psi for 30 min very limited deformation occurred for the various compositions. As discussed earlier in the discussions of flexural tests, plastic deformation at high temperatures appeared to increase with higher metal content. This trend was not observed in the compressive deformation experiments. At the low pressure of 2000 psi, all compositions exhibited similar resistance to creep. The effect of load is seen in the data for 50 Nb-31; at a higher load and longer time, much greater deformation resulted at a lower test temperature. These studies will be continued at higher temperatures, and test conditions will be varied within practical limits to determine the effects of load and time.

Machinability - With higher metal contents, some changes in machining procedure was necessary. While composites containing less than 50 vol% carbide could be sectioned using tools such as band saws, diamond wheels and grinders were necessary at metal levels of ≥ 70 wt% Nb. With diamond tooling, however, specimen preparation was relatively simple, and tolerance of $\pm .005$ could be maintained. Edges were very welldefined, and chipping did not occur.

C. Tantalum Carbide-Graphite System

Previous investigations of TaC-C had produced rather disappointing materials. At the 50 wt% level, flexural strengths were less than 2000 psi. However, this system has the highest carbide-carbon eutectic temperature reported (3450°C)⁷ and this high liquification temperature would make it a particularly desirable high temperature material. Study of this system was therefore pursued during this year's work. Processing temperatures for tantalum composites were raised as high as feasible in order

to exploit higher diffusion and sintering rates. Gross deformation of the graphite mold and plungers at temperatures higher than 3200°C precluded fabrications in the eutectic liquid range. However, results have shown that temperatures of $\geq 3100^{\circ}\text{C}$ enhances diffusion and sintering, yielding high strength composites. A summary of the data appears in Table V.

Microstructural Studies - Early experiments were concerned with the use of tantalum metal. It was felt that in forming the carbide, the metal might create a better bond with the graphite matrix. These pressings were carried out at 3000°C. The results for 50 Ta-A and 65 Ta (Table V) indicate poor bonding, and it is doubtful if any diffusion of carbide or carbide-graphite had occurred. Fairly high porosity and carbide grains undiminished in size are seen for 50 Ta-A (Fig 20b); the 65 Ta composite was quite similar in appearance. Evidently, 3000°C is too low a temperature (450°C below liquification point) for any appreciable diffusion bonding to take place.

Raising the processing temperature to 3100°C and use of the finer carbide raw material yielded the first TaC-C composites of significant strength (see data for 50 Ta). Microstructural examination shows a fine carbide dispersion and less porosity (Fig 20a). The data for a 60 wt% Ta composite (60 Ta in Table V) showed no improved bonding over 50 Ta. The carbide particles appeared somewhat coarser and the graphite matrix did not appear to be as dense (Fig 20c). This was surprising in that extent of densifications were about the same, i.e. 93.7% for 50 Ta and 94.6% for 60 Ta. It is possible that the processing temperature was actually higher for 50 Ta than for 60 Ta (although both were processed at an indicated 3100°C), and hence, better diffusion bonding resulted for the former.

Table V

SUMMARY OF TaC-C SYSTEM: FABRICATION DATA

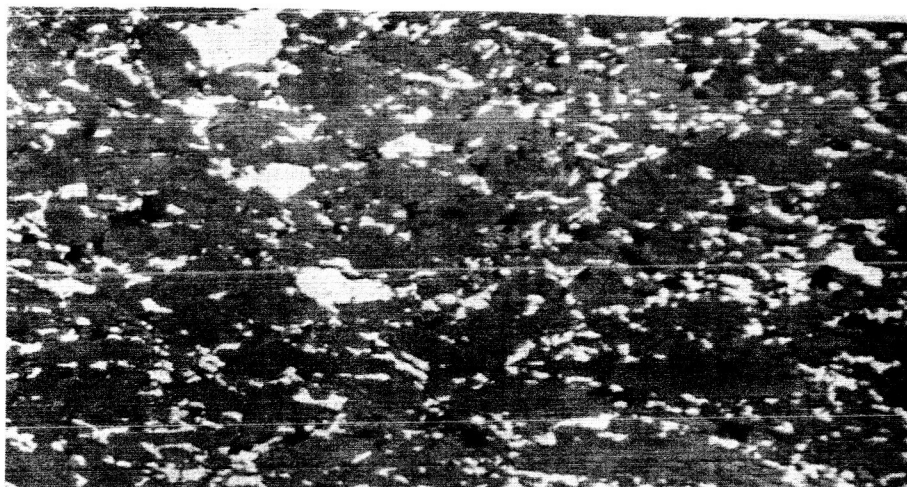
Compositional Designation	Form of Metal Addition	Pressing Temp, °C	Wt% Metal		Volume % Carbide	Density g/cc	%Theor. Density
			As Mixed	Actual			
50 Ta	Carbide	3100	50	50.4	15.3	3.88	93.7
50 Ta-A	Metal	3000	50	56.7	19.3	4.01	87.0
60 Ta	Carbide	3100	60	60.7	22.3	4.64	94.6
65 Ta	Metal	3000	65	--	26.1	4.97	91.4
65 Ta-A*	Carbide	3200	65	(a) 49.3 (b) 64.7	(a) 14.8 (b) 25.8	(a) 3.91 (b) 5.25	(a) 96.1 (b) 97.0
80 Ta	Carbide	3200	80	81.1	49.9	7.77	92.9
82.5 Ta	Carbide	3200	82.5	82.9	54.3	8.17	91.6
82.5 Ta-A	Carbide	3200	82.5	82.6	53.6	8.54	96.8
90 Ta	Carbide	3100	90	90.3	80.0	11.67	97.2

*Heterogeneous body. Upper portion of billet presented as (a) and lower portion as (b)

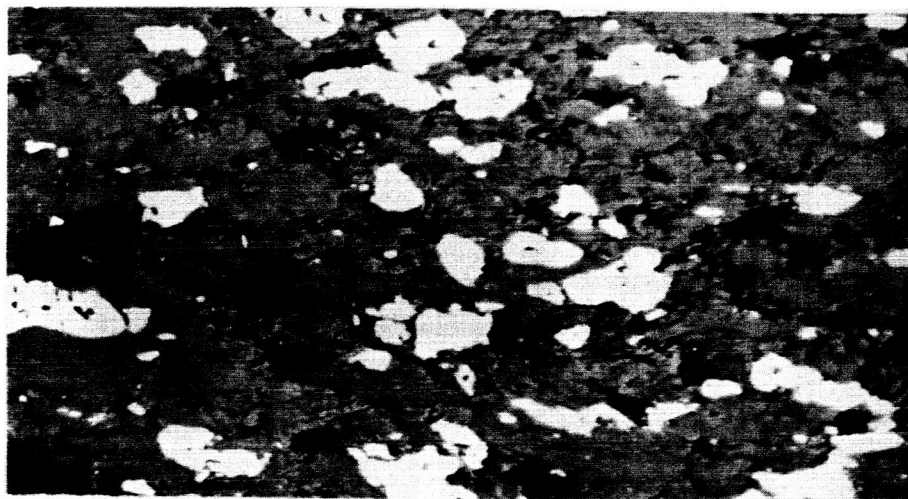
Table Va

SUMMARY OF TaC-C SYSTEM: PROPERTIES DATA

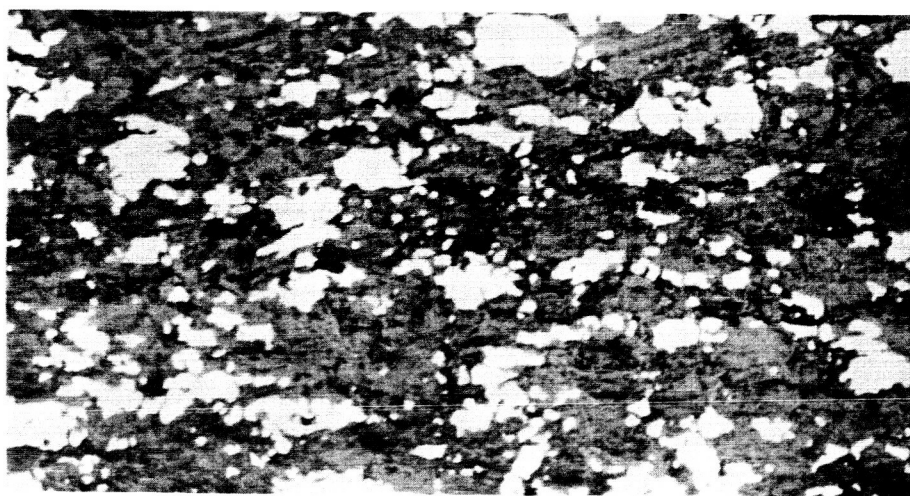
Compositional Designation	Flexural Strength, psi		Flexural Modulus x 10 ⁶ psi	Compressive Strength		Compressive Modulus x 10 ⁶ psi	Grain Direction
	Room Temp	2000°C	2500°C	psi	psi		
50 Ta	8,570	11,980	10,160	8,650	2.19	W/G	W/G
50 Ta-A	2,750	3,810	--	--	--	W/G	W/G
60 Ta	8,200	10,540	--	8,140	2.12	W/G	W/G
	3,200	3,340	--	13,300	1.00	A/G	A/G
65 Ta	3,130	6,450	--	--	--	W/G	W/G
	1,130	1,870	--	--	--	A/G	A/G
65 Ta-A	19,160	>22,460	20,900	10,300	2.07	W/G	W/G
	3,430	5,850	7,480	17,800	1.11	A/G	A/G
80 Ta	21,370	14,900	14,730	24,200	4.63	W/G	W/G
82.5 Ta	20,650	--	12,410	39,400	5.91	W/G	W/G
82.5 Ta-A	17,850	>23,940	17,660	46,100	5.26	W/G	W/G
	6,780	14,270	10,320	39,100	5.68	A/G	A/G
90 Ta	32,250	>32,000	22,800	117,400	7.50	W/G	W/G
	18,100	29,570	23,290	88,400	9.24	A/G	A/G



(a) 50 wt% Ta
Pressed at
3100°C
(50 Ta)*



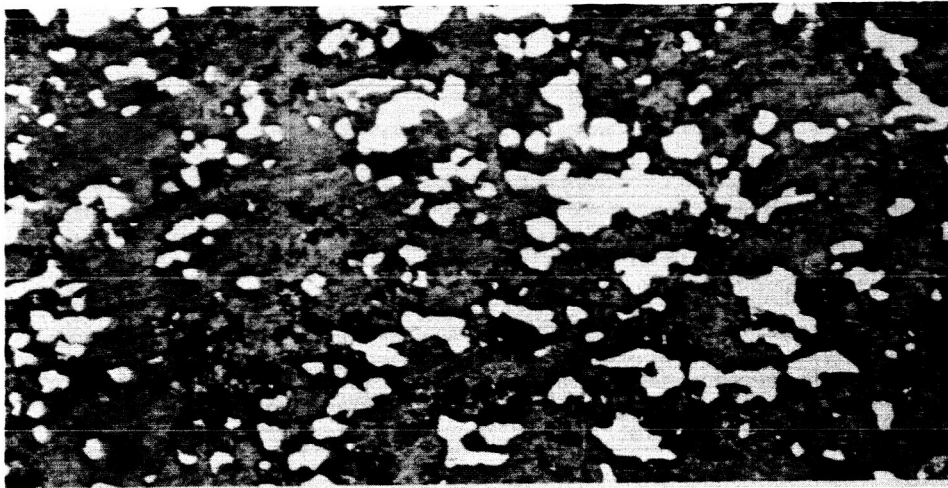
(b) 50 wt% Ta
Pressed at
3000°C
(50 Ta-A)*



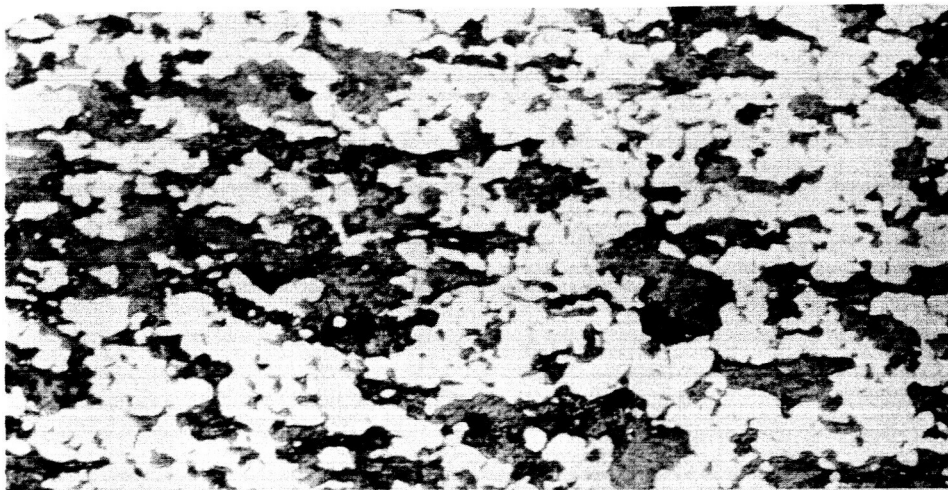
(c) 60 wt% Ta
Pressed at
3100°C
(60 Ta)*

* See Table VI

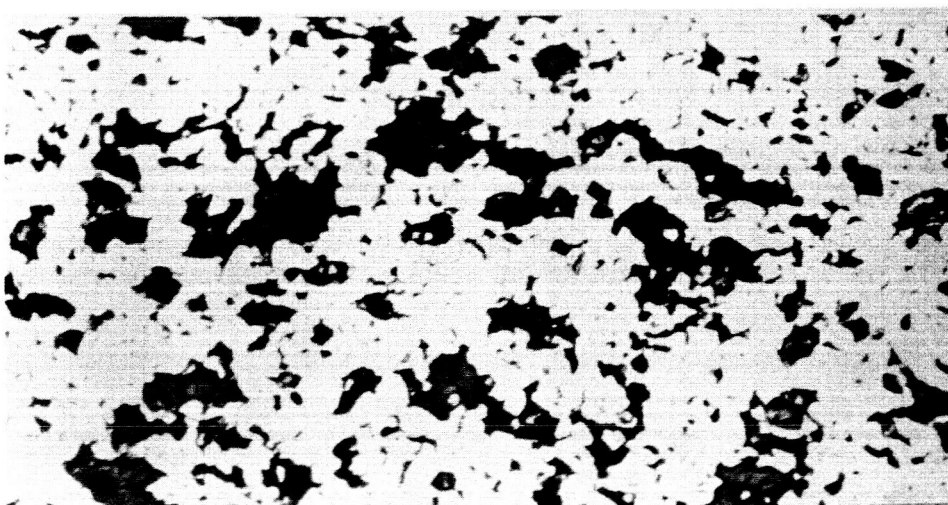
Fig 20 - MICROSTRUCTURE OF TaC-C COMPOSITES (320 X)



(d) 65 wt% Ta
Pressed at
3200°C
(65 Ta-A)*



(e) 82.5 wt% Ta
Pressed at
3200°C
(82.5 Ta-A)*



(f) 90 wt% Ta
Pressed at
3100°C
(90 Ta)*

* See Table VI

Fig 20 - MICROSTRUCTURE OF TaC-C COMPOSITES (320 X)

At a metal level of 82.5 wt%, continuity in the carbide phase begins to appear (Fig 20e). The volume levels of the two phases at this composition is about 50:50. The 90 wt% Ta billet appeared quite metallic to the eye and was the characteristic gold color of TaC. Fig 23f reveals the structure of this composition to be granite in a tantalum carbide matrix. X-ray diffraction patterns have revealed only the TaC phase; the Ta₂C structure is not present.

Physical Properties - The successful fabrication of high strength TaC-C composites has been a particularly satisfying aspect of this program. In terms of volume % carbide, compositions in this system have been found to be comparable in strength to corresponding composites in the niobium system. A graph of flexural strength vs temperature appears in Fig 21. In general, trends observed in the NbC-C studies were also observed for the TaC-C system. These are as follows:

1. Direct relationship between metal content and room temperature strength.
2. A maximum in strength at about 2000°C for the various compositions.
3. Direct relationship between metal content and plasticity at high ($\geq 2500^\circ\text{C}$) temperatures.

Some interesting properties were exhibited by the 65 wt% Ta composition (designated 65 Ta-A). This was the only composite in the TaC-C system which was heterogeneous; all of the others had density variations of less than 2%. However, strength data of the lower metal content or lower density specimens were within 5% of the higher metal content material and sometimes were actually higher. The strengths at the various test temperatures were quite high, comparing favorably with 50 wt% Nb which has about an equal volume % carbide content.

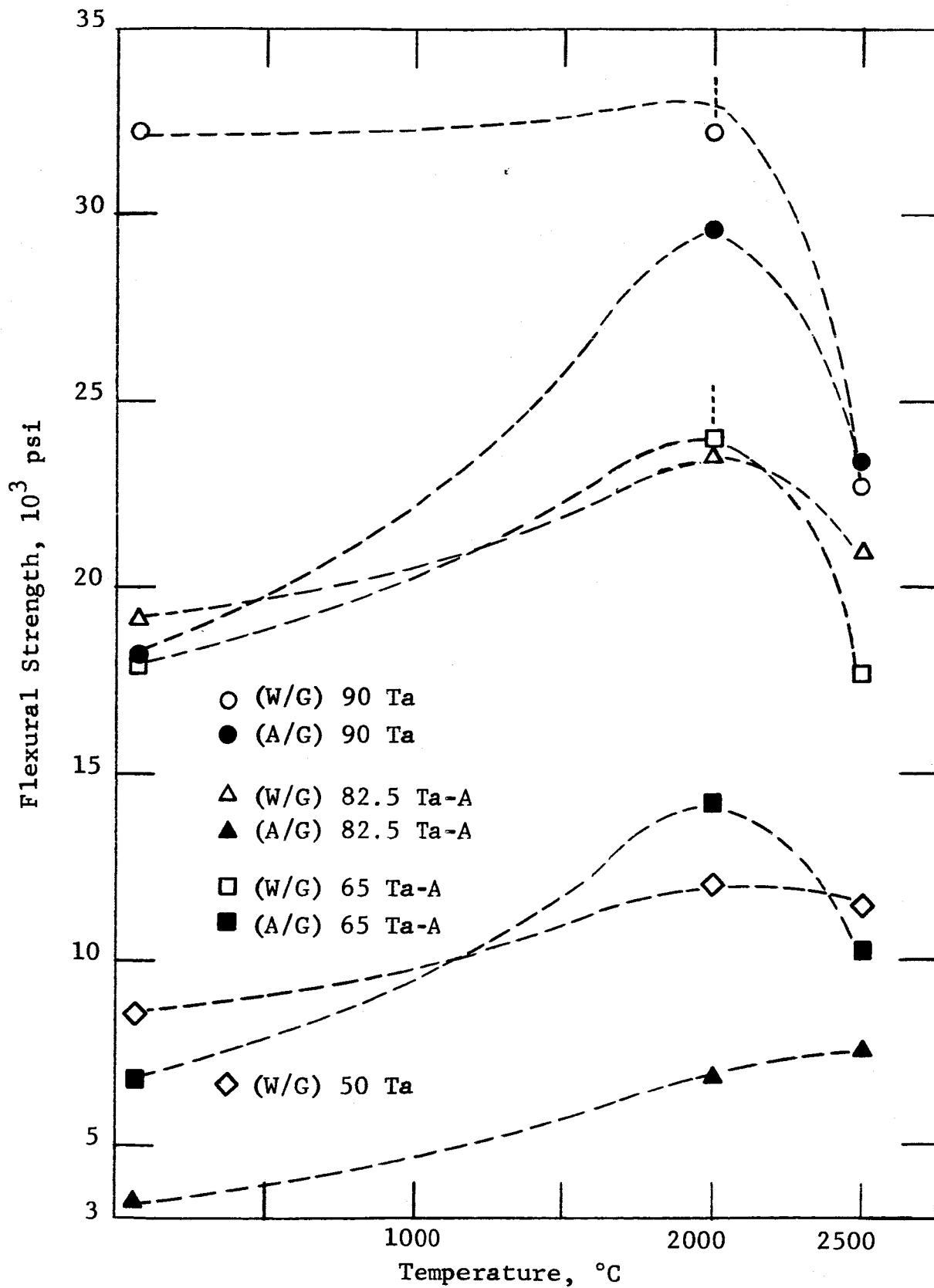


Fig 21 - HIGH TEMPERATURE FLEXURAL STRENGTH
OF TaC-C COMPOSITES

The 80 Ta and 82.5 Ta had high room temperature strengths but anomalously low high temperature strengths. The 82.5 Ta-A composition exhibited W/G strengths which were somewhat comparable to those for 65 Ta-A. However, the A/G strengths were substantially higher for 82.5 Ta-A, also revealing the trend toward isotropy at higher metal contents shown by the NbC-C system.

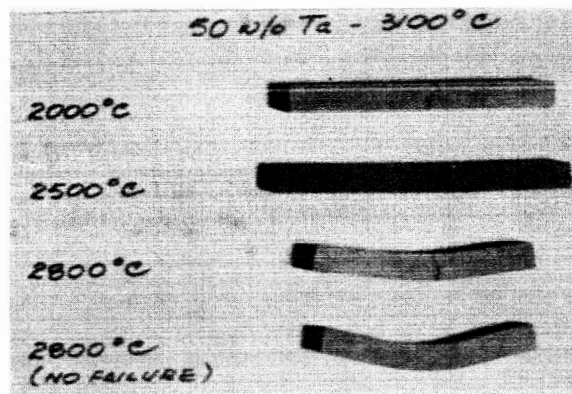
At the 90 wt% Ta level, very high strengths were observed for both grain directions. Again, the trend toward isotropic behavior at higher metal contents and at higher test temperatures was revealed. The ratios of W/G:A/G flexural strengths as a function of composition and temperature are as follow:

<u>Composition</u>	<u>Room Temp.</u>	<u>Test Temperature</u>	
		<u>2000°C</u>	<u>2500°C</u>
62.5 Ta-A	5.6	3.8	2.8
82.5 Ta-A	2.6	1.7	1.7
90 Ta	1.8	1.1	1.0

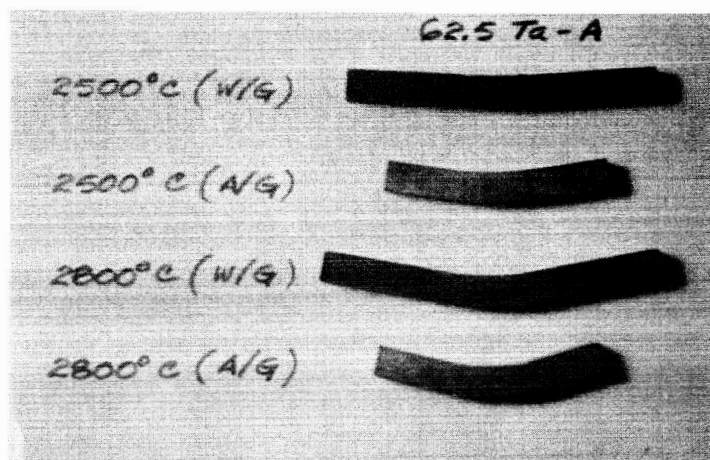
The 90 Ta composite was the highest strength composite fabricated on this program. This was also the hardest material produced. However, diamond tooling was sufficient for the machining of specimen shapes.

At a test temperature of 2800°C, TaC-C compositions exhibited behavior similar to that for NbC-C bodies, i.e., failure would occur for some samples while others deformed to the dimensional limitations of the flexural test apparatus prior to failure. For samples which were stressed to failure, the following strength levels were indicated: 50 Ta, 6870 psi; 80 Ta, 11,130 psi; 82.5 Ta-A, 12,800 psi (W/G) and 8120 psi (A/G).

Fig 22 shows the plastic behavior of flexural test specimens at higher temperatures. At 2000°C, all compositions exhibited

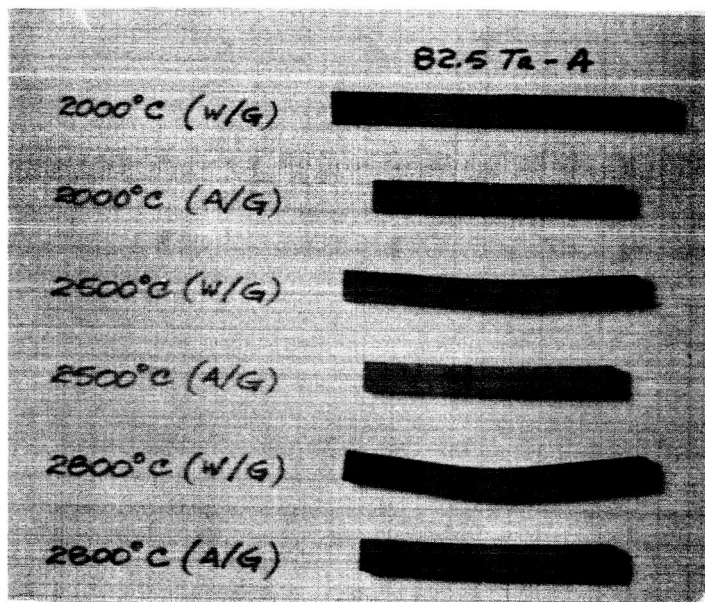


(a)

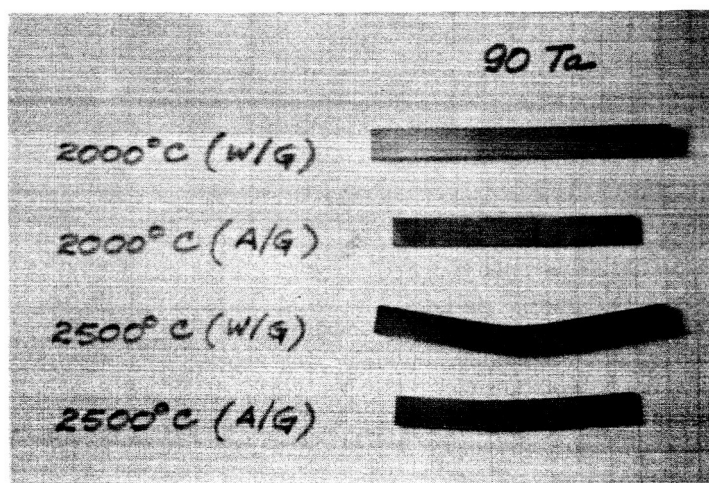


(b)

Fig 22 - HIGH TEMPERATURE FLEXURAL TEST SAMPLES
OF TaC-C COMPOSITES



(c)



(d)

Fig 22 - HIGH TEMPERATURE FLEXURAL TEST SAMPLES
OF TaC-C COMPOSITES

no deformation prior to failure. At 2500°C, the 50 wt% Ta revealed little if any plasticity. However, increasing plastic deformation was observed with increasing metal content. A rather curious phenomenon was observed for the higher metal content samples in terms of plasticity vs grain direction. As seen in Figs 22c, and 22d, the A/G specimens displayed less deformation prior to failure than did the W/G samples. At a lower carbide content of 65 wt% (Fig 22b) greater deformation occurred in the A/G than in the W/G direction, as was the case for other graphite matrix materials. This reversal in plastic behavior of the two grain directions at higher metal contents is not understood at this time.

Compressive strength was higher in the A/G direction than in the W/G direction for the graphite matrix composites (60 Ta and 65 Ta-A). This is similar to the directionality relationships for commercial ZT grade graphite which is prepared by hot pressing/working. At the higher metal contents, more isotropic behavior is exhibited as seen by the values for 82.5 Ta-A and 90 Ta. The general increase in elastic modulus as well as compressive strength with metal content is revealed by the values in Table V.

Experiments were conducted with various compositions in this system to determine resistance to compressive deformation at temperatures of $\geq 2500^{\circ}\text{C}$. The TaC-C samples revealed extremely modest dimensional changes at these temperatures (Table VI). Within the limited data available, it would appear that deformation was greater in the W/G direction than in the A/G direction. For 50 Ta, a higher load and longer time increased deformation. However, this increase was not as strong as for the NbC-C composition. Examination of the high temperature behavior of TaC-C composites will be continued and comparisons will be made to the NbC-C system.

Table VI
HIGH TEMPERATURE COMPRESSIVE DEFORMATION
OF TaC-C COMPOSITES

Compositional Designation	Composition Wt% - Metal	Pressing Temp °C	Grain Dir.	Test Conditions			$\frac{\Delta L}{L_0}$ %	$\frac{\Delta D}{D_0}$ %
				Temp, °C	Load, psi	Time, min		
50 Ta	50.4-Ta	3100	W/G	2500	4000	60	-2.2	--
50 Ta	50.4-Ta	3100	W/G	2600	2000	30	-1.6	+3.0
60 Ta	60.7-Ta	3100	W/G	2600	2000	30	+0.2	0
82.5 Ta-A	82.6-Ta	3200	W/G	2600	2000	30	-1.3	+2.2
			A/G	2500	2000	30	0	+0.3
90 Ta	90.3-Ta	3100	W/G	2550	2000	30	-0.6	+0.4
			A/G	2650	2000	30	-0.2	+0.7

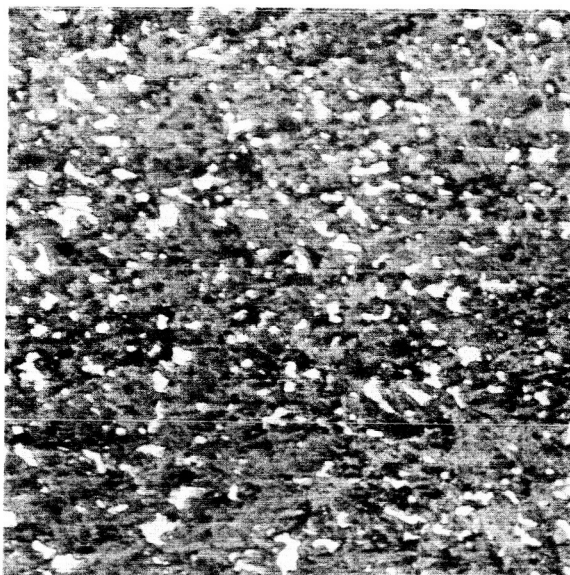
D. Molybdenum Carbide-Graphite System

Among the graphite matrix or low metal content composites in the different systems, the highest room temperature flexural strengths were exhibited by bodies incorporating molybdenum carbide. Strengths of greater than 17,000 psi exist for a variety of compositions with carbide contents as low as 8 volume percent. Investigations in this system were somewhat limited since the carbide-carbon eutectic of 2580°C ⁸ precludes its use at the very high temperatures. Discussion of this system and the other to follow will be presented in terms of experimental phases. The more extensive compositional studies in the NbC-C and TaC-C systems suggested that they be discussed in the broader categories of microstructure and mechanical properties.

Effect of Processing Temperature and Time - Experiments were performed to determine the effect of soak time at temperature on the properties of molybdenum carbide-graphite composites. Two processing temperatures, 2800° and 3000°C , and two soak times, 0 and 1 hr were introduced as variables for 50 wt% Mo compositions. The results are summarized in Table VII. The effects of a one hour soak are as follows:

1. No significant change in room temperature strength was apparent.
2. Densities are somewhat lower after a one hour soak. This was due to loss of metal, resulting in composites of less than 50 wt% Mo as detailed in Table VII.
3. Anisotropy increased after a one hour soak, revealing a higher degree of ordering.

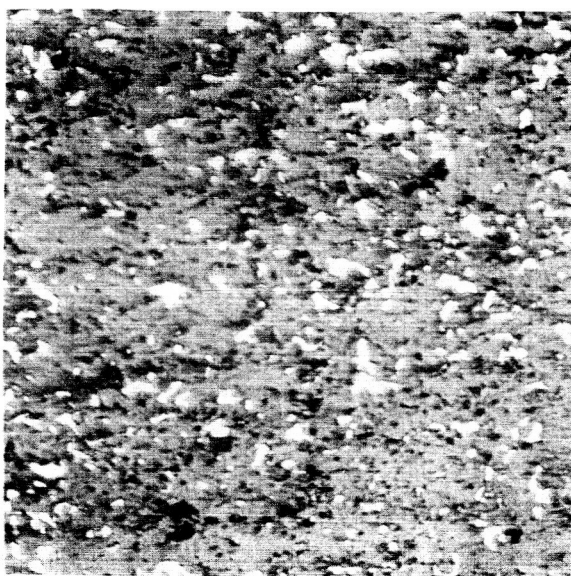
The higher processing temperature, i.e., 3000°C vs 2800°C resulted in bodies of slightly lower densities and strength. This was due to greater loss of metal, an effect also seen after a one hour soak as listed above. Microstructural examination (Fig 23) shows the decreasing amounts of carbide with higher processing temperature and longer soak times. Despite



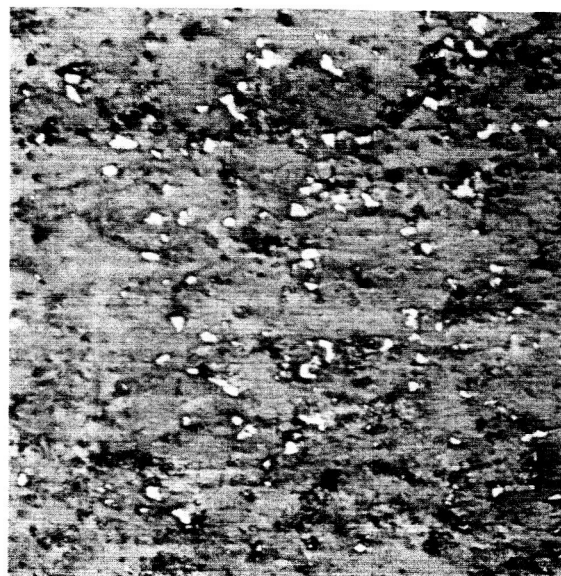
(a) Pressed at 2800°C
(Mo-28)*



(b) Pressed at 2800°C,
1 hour soak
(Mo-28/1)*



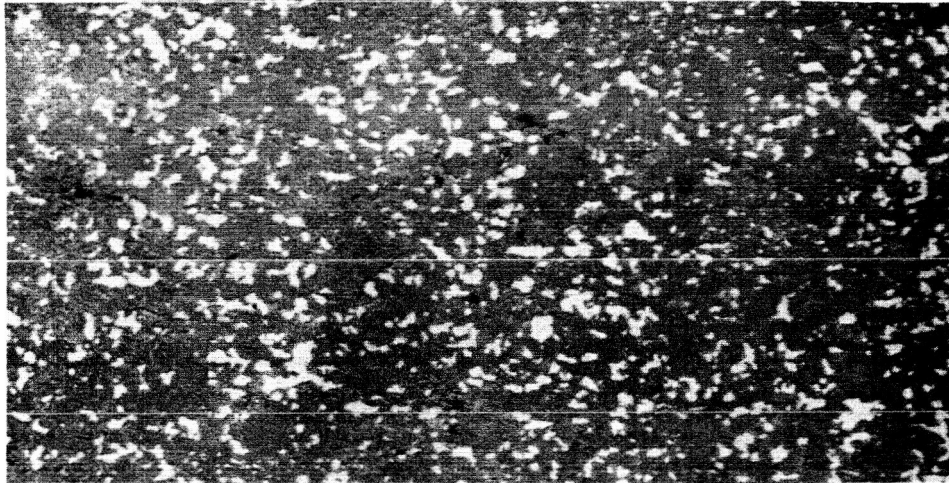
(c) Pressed at 3000°C
(Mo-30)*



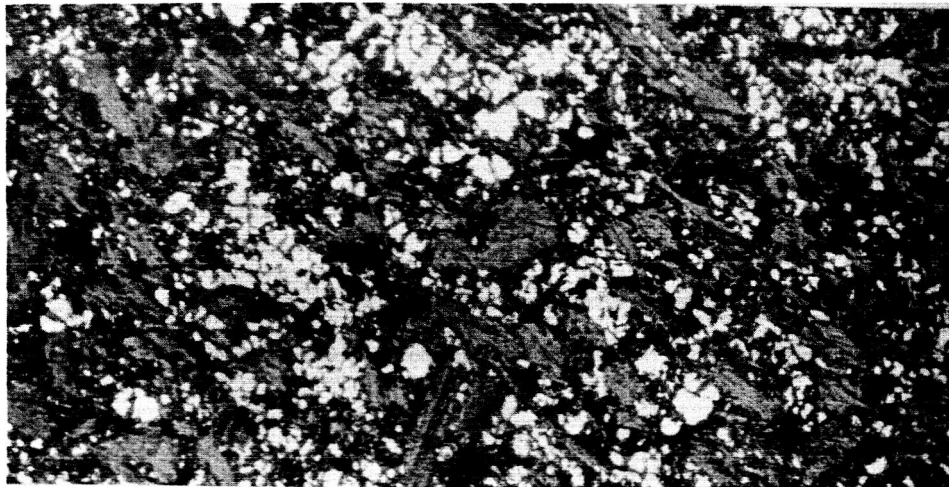
(d) Pressed at 3000°C,
1 hour soak
(Mo-30/1)*

* See Table VII

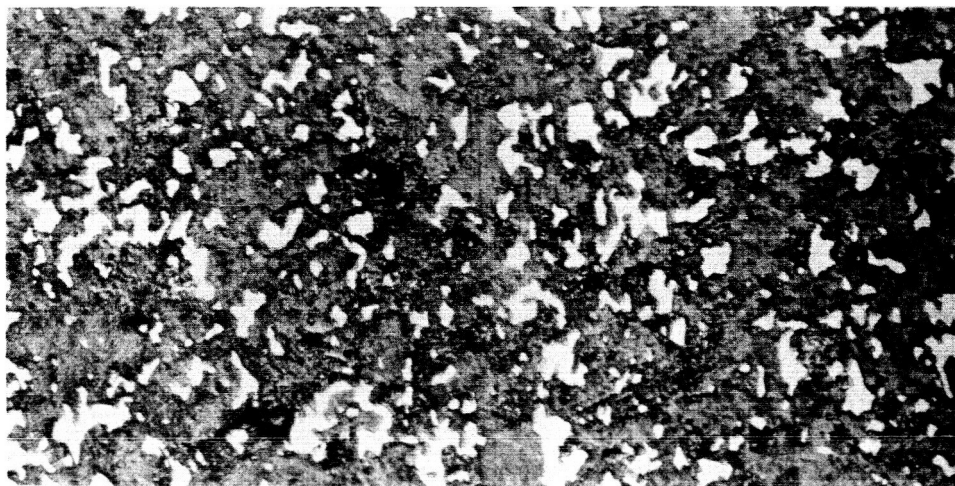
Fig 23 - MICROSTRUCTURE OF MOLYBDENUM CARBIDE-
GRAPHITE COMPOSITES (320 X)



(e) Pressed at
2600°C, 1
hour soak
(Mo-26)*



(f) LASL Composite,
Upper Portion
of Billet
(50 wt% Mo,
Vacuum Hot
Pressed at
2800°C)



(g) LASL Composite,
Lower Portion
of Billet
(50 wt% Mo,
Vacuum Hot
Pressed at
2800°C)

*See Table VII

Fig 23 - MICROSTRUCTURE OF MOLYBDENUM CARBIDE-
GRAPHITE COMPOSITES (320 X)

Table VII

SUMMARY OF MOLYBDENUM CARBIDE-GRAPHITE SYSTEM

FABRICATION DATA:						
Compositional Designation	Pressing Temp, °C	Soak Time	Actual Metal Content, Wt%	Volume % Carbide	Density g/cc	% Theoretical Density
Mo-26	2600	1 hr	38.5	14.7	3.10	95.4
Mo-28	2800	0	39.0	14.9	3.12	95.4
Mo-28/1	2800	1 hr	34.8	12.7	2.97	95.2
Mo-30	3000	0	34.7	12.7	2.97	95.5
Mo-30/1	3000	1 hr	27.5	8.2	2.75	95.2
PROPERTIES DATA:						
Compositional Designation	Flexural Strength, psi					
	Room Temperature			2000°C		
	W/G	A/G	W/G:A/G	W/G	A/G	% Loss in Strength at 2000°C
Mo-26	19,040	--	--	15,670	--	17.7
Mo-28	18,930	6740	2.8	13,840	Creep	26.9
Mo-28/1	19,150	6390	3.0	14,720	Creep	23.1
Mo-30	17,800	6450	2.8	14,690	Creep	17.5
Mo-30/1	17,020	5050	3.4	15,380	Creep	9.6

the variations in amount of metal lost for the various composites, the degree of densification (see % Theoretical Density column in Table VII) was virtually the same for all of the compositions.

Unlike the tantalum or niobium compositions, all samples exhibited strength losses at 2000°C in the W/G direction and creep in the A/G direction. There did appear to be a definite correlation between this loss in strength and both processing temperature and time of soak. As shown in Table VII, retention of strength was better for samples which had been soaked, and also for those fabricated at the higher (3000°C) temperature. At a 2500°C test temperature only the sample of lower metal content (Mo-30/1) could be stressed to failure (14,000 psi); the others exhibited considerable plastic deformation and a load of 25,000 psi was attained without failure. Although the carbide contents studied in this system are considerably lower than those of TaC-C of NbC-C, the trend toward high temperature plasticity with higher metal contents appear to be analogous.

Effect of Heat Treatment - During mechanical property evaluations at 2500°C, it was seen that some of the molybdenum composites formed droplets on the surfaces of the test specimens. Experiments were conducted to investigate this phenomenon. The samples listed in Table VII processed at 2800°C, 2800°C/1 hr, 3000°C, and 3000°C/1 hr were subjected to a temperature of 2600°C for two hrs. "Sweating" occurred most strongly for the Mo-28, or the highest metal content samples, and did not occur in the Mo-30/1 hr samples. The weight losses were: Mo-28, 3.22%; Mo-28/1hr, 1.19%; Mo-30, 1.80%; and Mo-30/1 hr, 0.11%.

Shown in Fig 24, is a "sweated" sample and microstructural examination of the cross section of a bubble. The area directly under the exuded carbide bubble shows dense graphite and large carbide particles. X-ray examination revealed the bubble to

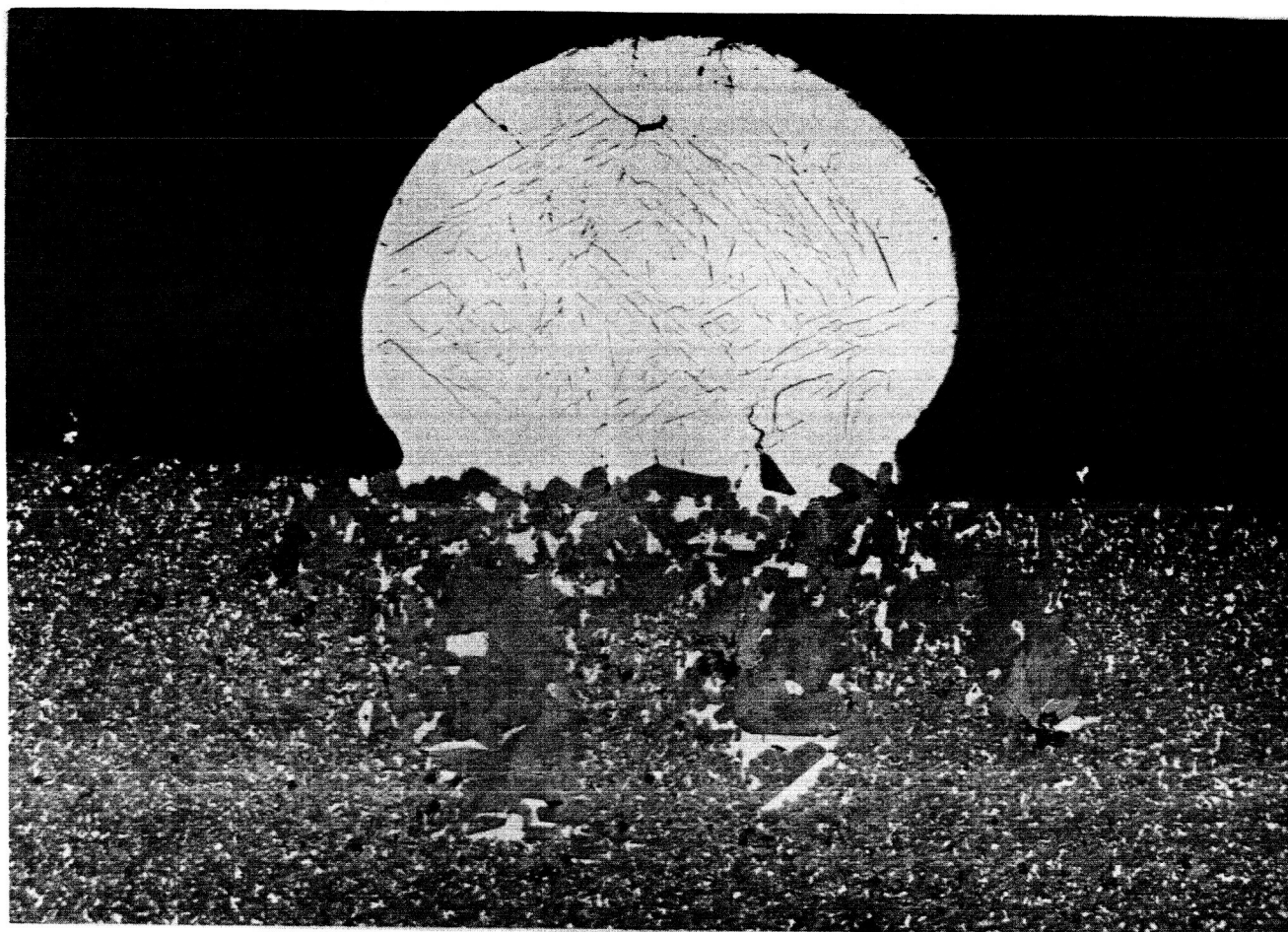
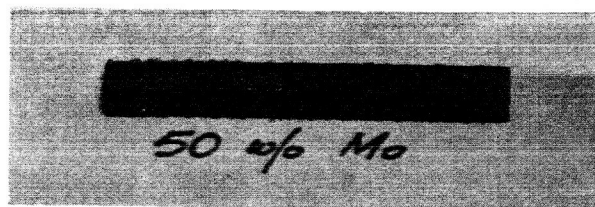


Fig 24 - MICROSTRUCTURE OF "SWEATED" AREA
IN Mo-28 SAMPLE, HEAT TREATED AT
2600°C/2 HOURS (100 X)

be primarily Mo_2C with small amounts of MoC and C. It would appear that the Mo_2C phase coalesces and finally escapes the parent body, leaving behind a highly oriented graphite phase as indicated by the same area under polarized light (Fig 25). The high degree of ordering and strong bond obtained in brazing of graphite as observed at Los Alamos and Westinghouse may be due to this type of mechanism. It may be possible to exploit this behavior in producing graphites of high density and strength.

Vacuum vs Atmospheric Hot Pressing - As described in the section entitled "Preparation and Fabrication," hot pressings at IITRI have been conducted essentially at atmospheric pressure. A 50 wt% Mo composition was fabricated at LASL by a 2800°C vacuum hot pressing so that a comparison might be made between vacuum and atmospheric (reducing conditions) processing. Raw materials were furnished by IITRI; heating and cooling rates and pressures were maintained as close to those used at IITRI to minimize processing variables.

Initial examination of the LASL composite revealed two differences from IITRI bodies: little if any reaction with the mold and plungers was evident, and diametral deformation was considerably less. Sectioning of the billet revealed what appeared to be a two phase system. The upper portion was quite dark in color and rather soft, and the lower portion was lighter in color and much harder. A distinct line of separation rather than a gradation was evident. Pertinent data are as follows:

	Density g/cc	Actual Metal Content, wt%	%Theoret- ical Den- sity	Flexural Strength psi
Upper Portion	2.94	54.0	74.1	3090
Lower Portion	3.56	52.8	91.0	16,060

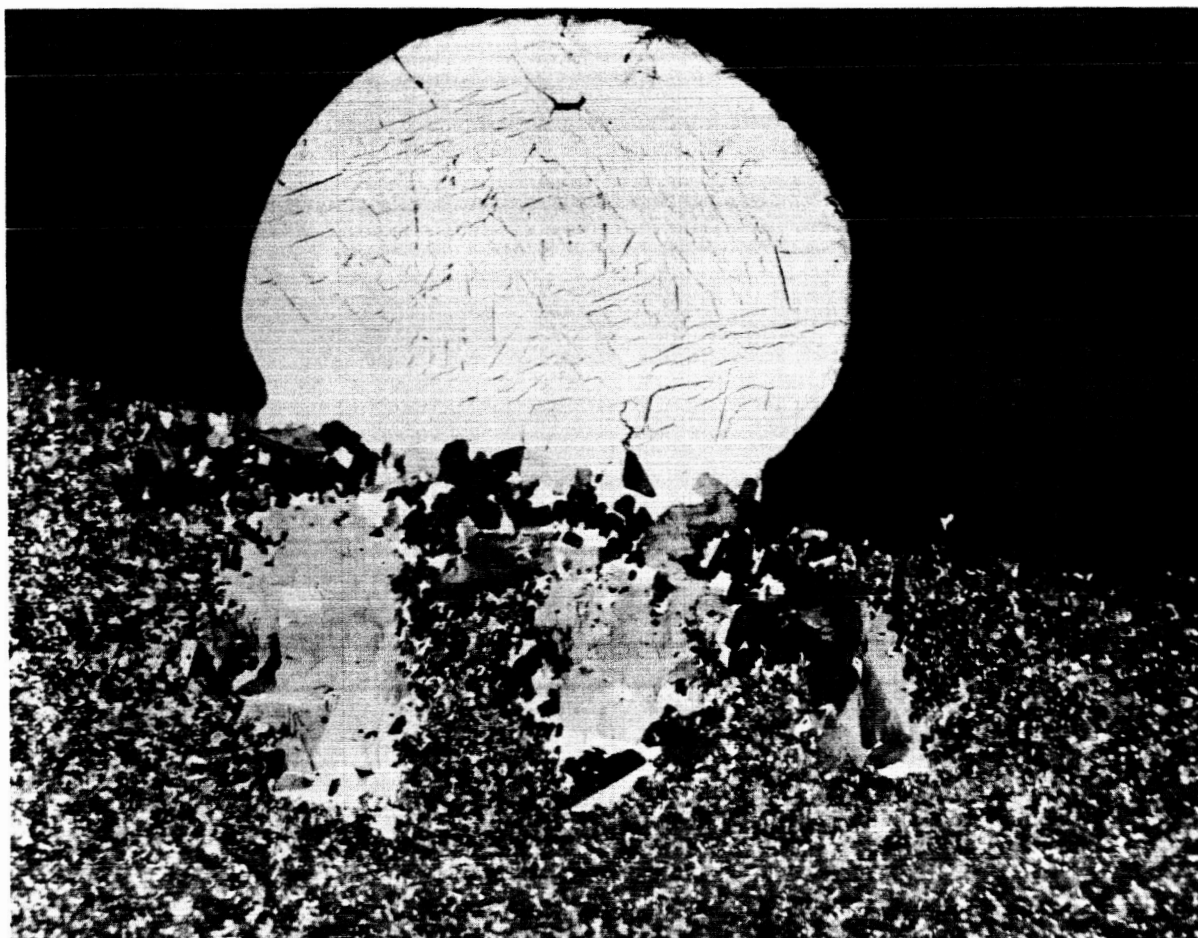


Fig 25 - MICROSTRUCTURE OF "SWEATED" AREA
IN Mo-28 SAMPLE, HEAT TREATED AT
2600°C/2 HOURS (POLARIZED LIGHT, 100 X)

It is evident from this data that the upper portion had not sintered to any great extent. Microstructural examination shows that the upper portion (Fig 23f) is quite porous with little densification of the graphite matrix. The lower portion (Fig 23g) is similar to the IITRI Mo-28 although the carbide grains appear somewhat larger.

Metal analyses revealed surprisingly that no metal had been lost. The comparable Mo-28 had shown a 39 wt% metal content. It would appear that the temperature of the LASL pressing may not have been as high as that used at IITRI for Mo-28. The lack of densification in the upper portion may be due to inadequate pressure transfer in the upper plunger. A repeat of this experiment appears advisable for a more valid comparison between the processing methods, i.e. vacuum vs atmospheric.

E. Zirconium Carbide-Graphite System

The zirconium system exhibited only limited bonding and densification in previous work on this program (~5000 psi). However, the ZrC-C eutectic temperature of 2910°C ⁹ would make it seem ideal for liquid phase sintering at processing temperatures of 2800° or 3000°C , so new composites were prepared and processed at both temperatures. The results show the importance of processing at a temperature lower than the eutectic in order to obtain dense, high strength composites. This system is summarized in Table VIII.

Effect of Processing Temperature - Composites containing 50 wt% Zr were hot pressed at 2800° and 3000°C . As the data in Table VIII show, the sample (50 Zr-28) processed below the eutectic temperature exhibited good bonding (13,000 psi) and densification. The 50 Zr-30 fabricated at 3000°C had lower strengths which were similar to the values of ~5000 psi obtained in the earlier program. Metal analysis revealed that only 16 wt% metal remained in this composite.

Table VIII

SUMMARY OF METAL CARBIDE-GRAPHITE SYSTEMS: FABRICATION DATA

Compositional Designation	Form of Metal Addition	Pressing Temp °C	Wt% Metal		Volume % Carbide	Density g/cc	%Theor. Density
			As Mixed	Actual			
50 Zr-28	Carbide	2800	50	48.3	29.2	3.32	94.1
50 Zr-30	Carbide	3000	50	16.1	7.1	2.22	86.4
65 Zr-30	Carbide	3000	65	17.9	8.0	2.12	81.2
80.7 Zr	Carbide	2800	80.7	79.5	75.4	5.55	99.3
50 ZrO ₂	Oxide	2800	50	21.0	9.6	2.41	89.9
50 Ti-26	Carbide	2650	50	44.5	36.7	3.03	93.5
50 Ti-28	Carbide	2800	50	17.3	11.3	2.04	79.7
50 V-26	Carbide	2600	50	26.2	15.7	2.46	87.2
50 V-30	Carbide	3000	50	28.2	17.2	2.29	79.8
50 W-30	Metal	3000	50	48.9	13.5	3.70	90.7
65 Hf-30	Carbide	3000	65	65.1	28.7	4.99	94.7

Table VIIia

SUMMARY OF METAL CARBIDE-GRAPHITE SYSTEMS: PROPERTIES DATA

Compositional Designation	Flexural Strength, psi		Flexural Modulus x 10 ⁶ psi	Compressive Strength psi	Compressive Modulus x 10 ⁶ psi	Grain Direction
	Room Temp	2000°C				
50 Zr-28	13,390	18,750	12,620	12,610	3.39	W/G
50 Zr-20	5,810	12,710	--	--	--	W/G
65 Zr-30	4,400	7,280	--	--	--	W/G
80.7 Zr	16,910	22,340	11,270	99,600	15.17	W/G
50 ZrO ₂	7,540	--	--	--	--	W/G
50 Ti-26	13,630	12,290	Creep	14,400	2.30	W/G
	5,020	5,420	Creep	17,300	1.51	A/G
50 Ti-28	5,570	--	--	--	--	W/G
50 V-26	16,710	16,980	11,900	8,540	1.94	W/G
50 V-30	4,710	7,200	--	--	--	W/G
50 W-30	15,100	15,810	--	7,470	--	W/G
	5,030	Creep	--	17,110	--	A/G
65 Hf-30	10,130	11,810	15,840	8,510	2.90	W/G

Approximately 65% of the metal (as the carbide) had been lost through extrusion around the plungers and reaction with the mold. In addition, examination of the billet revealed macropores which would act as flaws. These voids may have resulted during recrystallization shrinkage of fairly large volumes of melt.

Microstructural examination of 50 Zr-30 (Fig 26a) and 50 Zr-28 (Fig 26b) confirms the much lower carbide content in the 3000°C material. The fine dispersion and lack of orientation suggests that melting and recrystallization had occurred. In contrast, the carbide grains in 50 Zr-28 are considerably larger, oriented, and somewhat angular in shape, thus indicating little evidence of melting.

The significant loss of metal and poor bonding which can occur by processing at too high a temperature is evident for 50 wt% Zr bodies. Composites of 50 wt% Mo processed well above its eutectic did not show such gross material loss or lack of bonding as described in the preceding section. This may be due to two reasons. First the total volume percent represented by the eutectics in the composites would be about 40% for 50 wt% Zr and 26% for 50 wt% Mo. Thus the zirconium composite would have more of the mobile liquid phase. Secondly, in the raw form prior to processing, the Mo metal powder is much finer than zirconium carbide. Therefore, the probability of coalescing of melt phase into larger volumes exists, and upon recrystallization, segregation and voids can occur.

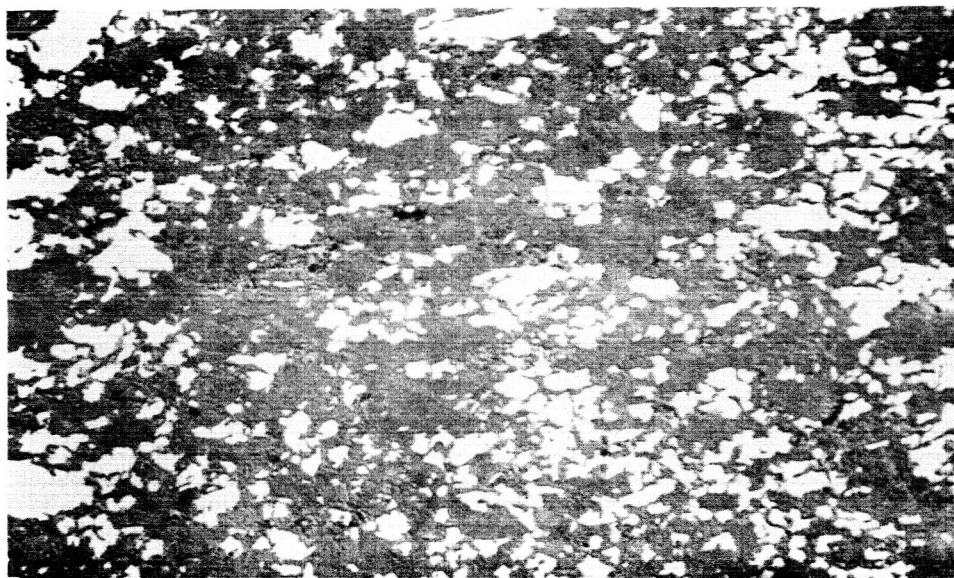
A 3000°C processing temperature yielded a composite of 65 wt% Zr which was similar to the 50 wt% Zr hot pressed at 3000°C, i.e. gross loss of metal and poor bonding.

A eutectic composition was also processed at 2800°C. This sample (80.7 Zr) exhibited high strengths, and analysis of metal content revealed a very small loss. The microstructure of this composite (Fig 27a) shows free graphite, and carbide-carbon solution to yield the eutectic structure appears quite limited.

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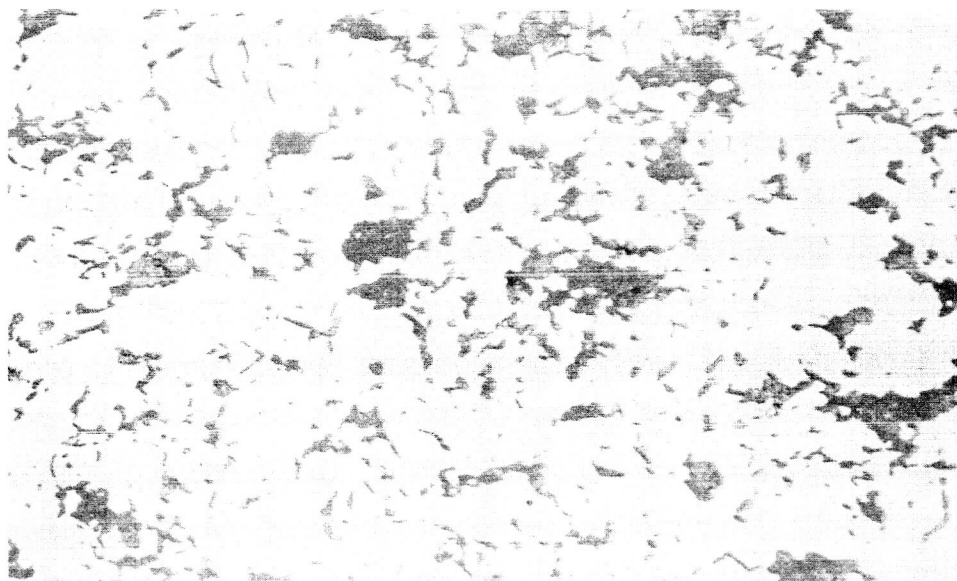
(a) Pressed at 3000°C (50 Zr-30)*



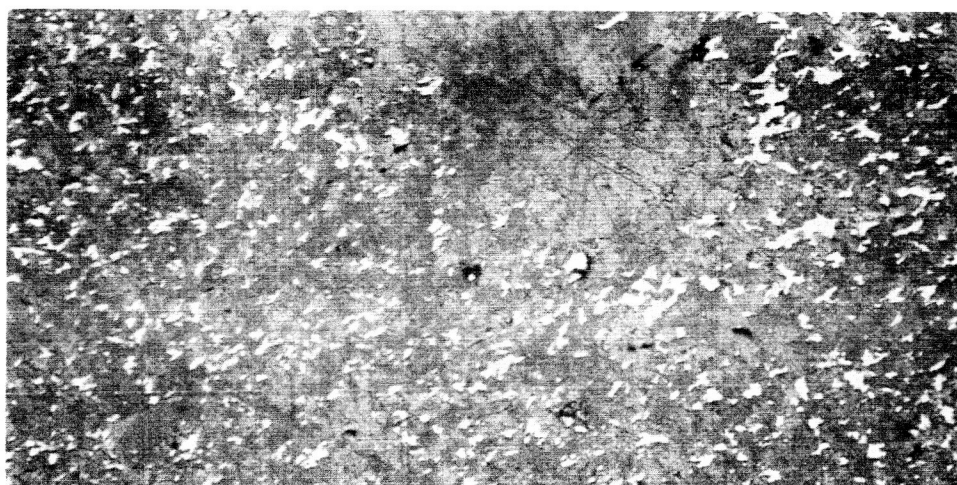
(b) Pressed at 2800°C (50 Zr-28)*

* See Table VIII

Fig 26* - MICROSTRUCTURE OF 50 WT% Zr COMPOSITES (320 X)



(a) 80.7 wt% Zr Pressed at 2800°C
(80.7 Zr)*



(b) 50 wt% Zr Pressed at 2800°C Using ZrO_2
(50 ZrO_2)*

*See Table VIII

Fig 27 - MICROSTRUCTURE OF ZrC-C COMPOSITES (320 X)

Fig 28 illustrates the relationship between flexural strength and temperature for the ZrC-C system. The compositions processed at 2800°C displayed a significant increase in strength at 2000°C but a strong dropoff at 2500°C. The higher metal content composition (80.7 Zr) displayed a larger loss and was actually weaker (11,300 psi vs 12,600 psi) than 50 Zr-28 at 2500°C. This effect of metal content on high temperature strength parallels the behavior of niobium compositions. At a test temperature of 2600°C, extensive plastic deformation was observed for 50 Zr-28.

A very high compressive strength (~100,000 psi) was exhibited by 80.7 Zr. Fig 29 shows a classical compressive failure for one of the samples of this composition. The resistance to compressive deformation of a 50 Zr-28 sample was examined under test conditions of 4000 psi/2500°C/60 min. A linear change of 12.5% was observed; under identical conditions, the 50 Nb-31 and 50 Ta samples exhibited deformations of 6.2 and 2.2% respectively (see Tables IV and VI). Apparently zirconium carbide composites are not as resistant to high temperature deformation as compositions incorporating NbC or TaC. As is seen by data for other systems described later, a direct relationship appears to exist between high temperature plasticity and liquification temperature of the system.

Use of ZrO_2 as the Metal Source - Attempts were made to fabricate bodies substituting ZrO_2 for the carbide as the metal source. The oxide was available in a much finer form than the carbide. It was felt that when the oxide reacted with the carbon during hot pressing, a fine dispersion of the carbide in the graphite matrix could be obtained. This is particularly important in lower metal content samples in which such a fine dispersion has been found to aid in densification and good bonding.

The fabrication procedure consisted of a 30 min hold at 1800°C to permit the oxide-carbon reaction to occur, and a final processing temperature of 2800°C. Initiation of the metal oxide-carbon reaction is listed at 1700°C - 1800°C.¹⁰ During the

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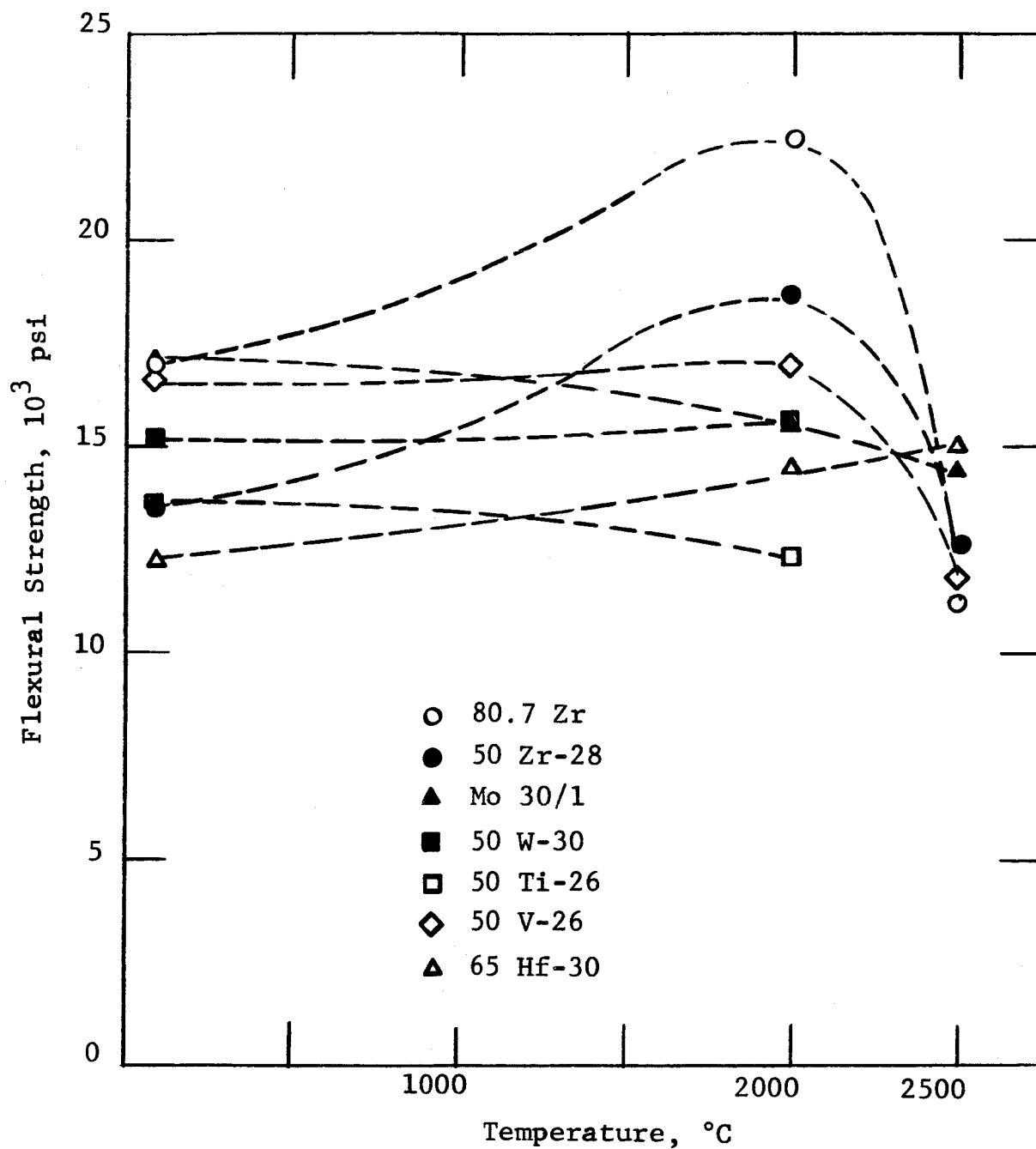


Fig 28 - HIGH TEMPERATURE FLEXURAL STRENGTH
OF METAL CARBIDE-GRAPHITE COMPOSITES

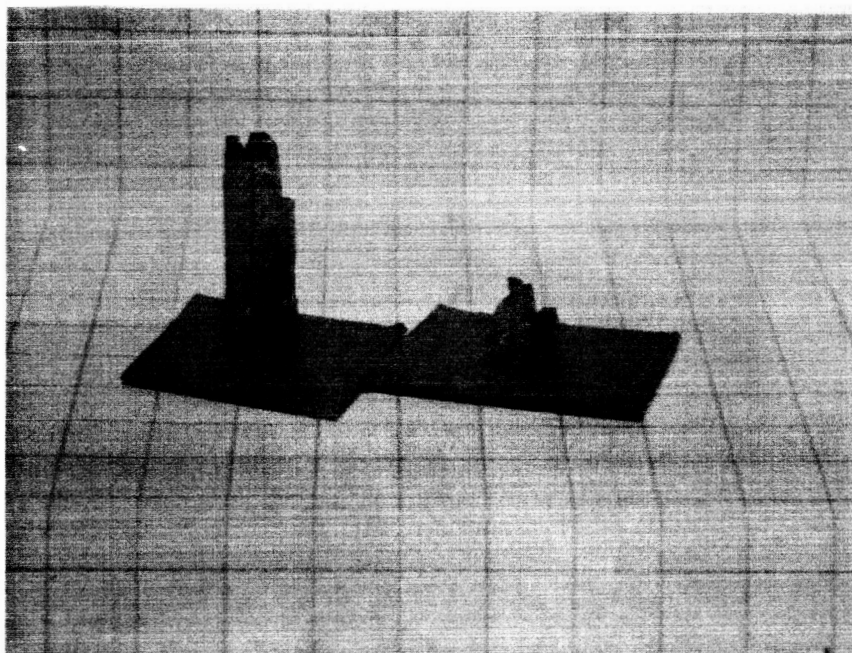


Fig 29 - COMPRESSIVE TEST SPECIMEN OF 80.7 Zr SHOWING
CLASSICAL BRITTLE FAILURE

processing, substantial evolution of gases (CO and CO₂) from the oxide-carbon reaction was evident. As shown in Table VIII for 50 ZrO₂, both density and flexural strength were relatively low as compared to those for a similar composition utilizing carbide (50 Zr-28). Metal loss was also significant. Microstructural examination (Fig 27b) revealed a fine but somewhat heterogeneous dispersion of the carbide phase and also the presence of large pores. The pressures exerted by the volatiles which were released during the reaction to form the carbide were apparently strong enough to physically move material and cause non-uniformity in metal dispersion.

Future experiments employing oxides will consider moderation of the oxide-carbon reaction. This can be accomplished by lowering the reaction temperature from 1800°C to about 1500°C, soaking at the initial plateau temperature for longer times, or pre-reacting the raw materials prior to actual hot pressing. This should prevent excessive loss of material and segregation which are detrimental to physical properties.

Vacuum vs Atmospheric Hot Pressing - The vacuum vs atmospheric hot pressing experiments reported earlier for molybdenum composites was also conducted with 50 wt% Zr compositions. This composition was also processed LASL under vacuum, keeping all other variables constant.

Evaluation of the zirconium body showed a heterogeneity similar to that for the molybdenum composite, i.e. higher density toward the lower portion of the billet. Data for the LASL 50 wt% Zr are as follow:

	Density g/cc	Actual Metal Content wt%	% Theoretical Density	Flexural Strength, psi
Upper Portion	3.05	50.2	84.5	2920
Lower Portion	3.32	50.3	92.0	6870

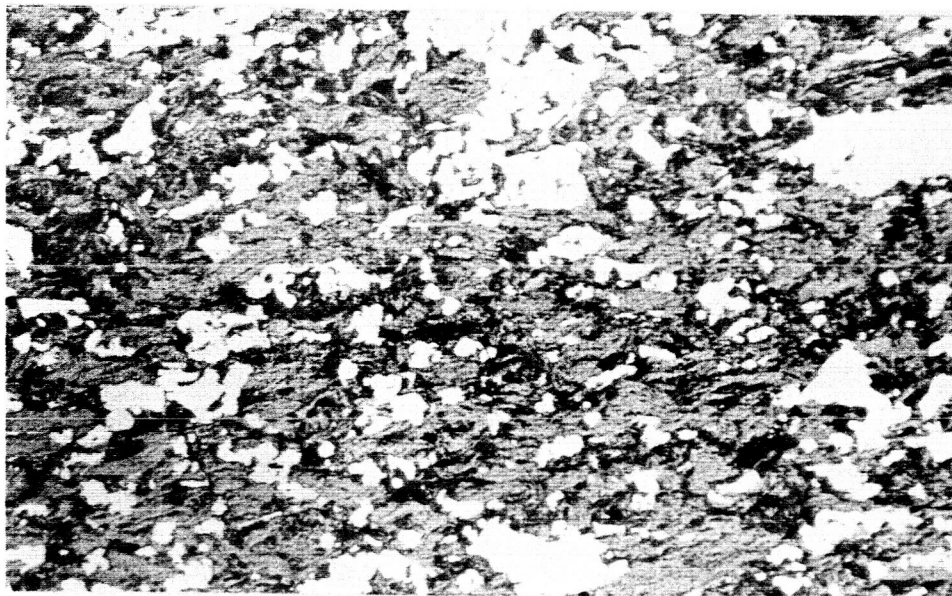
Despite having about the same metal content as the lower portions, the samples sectioned from the upper portions were of lower density and exhibited poor bonding. The denser lower portions were of higher strength but were considerably weaker than composites prepared at IITRI (50 Zr-28, 13,000 psi). Metallographic examination revealed the graphite matrix to be fairly porous and of a grainy structure (Fig 30). Similar to the molybdenum studies, it would appear that temperatures were not high enough for diffusion bonding and/or pressures were not completely applied on the billet during processing.

F. Metal Carbide-Graphite Systems: TiC-C,
VC-C, WC-C and HfC-C

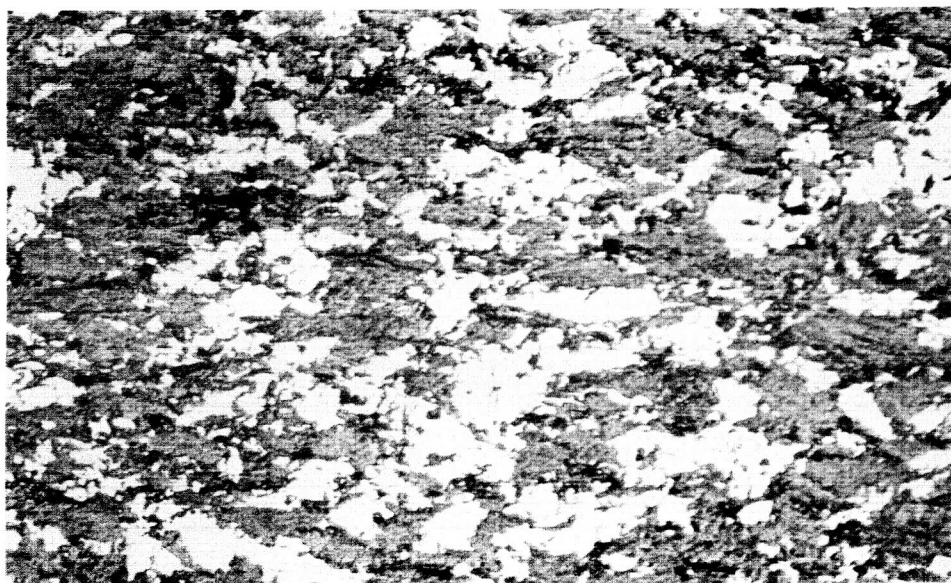
The systems discussed in this section were not studied as extensively as were NbC-C and TaC-C. Emphasis on this program had been placed on niobium and tantalum systems since they exhibited the greatest promise for high temperature use. Experiments conducted with TiC-C and VC-C have shown that processing below the liquification temperature yield dense, high strength composites. Tungsten was included in this year's studies, and results show that densification and bonding attainable in this system are similar to that for molybdenum carbide-graphite. The data for these various compositions appear in Table VIII.

Effect of Processing Temperature - The eutectic temperature in the TiC-C system is reported as 2775°C ⁹ and the melting point of VC is listed as 2650°C .⁷ Hot pressing of 50 wt% compositions in these systems at temperatures above the liquidus yielded bodies of low strength (~5000 psi) as seen by the data for 50 Ti-28 and 50 V-30 in Table VIII. Substantial loss of metal also occurred in both compositions.

When these same compositions were processed below their respective liquification temperatures, high strength (>10,000 psi) samples were obtained (50 Ti-26 and 50 V-26). Metal loss was



(a) Upper Portion of Billet



(b) Lower Portion of Billet

Fig 30 - MICROSTRUCTURE OF ZrC-C COMPOSITE
VACUUM HOT PRESSED AT 2800°C (320 X)

minimized in the titanium system. The difference between processing above or below the liquification temperature appears to be the same for TiC-C as for ZrC-C. At the 50 wt% metal level, about 56 volume percent would be TiC-C eutectic liquid. The mobility and reactivity of this liquid phase apparently leads to gross loss of carbide and to subsequent low strengths.

In the vanadium system, metal loss was about the same at both processing temperatures. However, the bonding was obviously superior for the body fabricated at 2600°C (16,000 psi vs 5,000 psi). Density measurements show that extent of densification was substantially higher for 50 V-26 (87%) than for 50 V-30 (80%), indicating lesser porosity and/or a denser graphite matrix for the former.

Processing of 50 wt% W at 3000°C, which is over 200°C higher than the 2776°C¹¹ melting point of WC, did not result in extensive loss of metal as was the case for 50 wt% Zr or 50 wt% Ti. The density of WC is quite high (15.8 g/cc) and a 50 wt% metal level corresponds to only 14 volume percent carbide (see Fig 8). Thus the amount of liquid which would be present for 50 wt% W at the high fabrication temperatures would be considerably less than for 50 wt% Zr (~40 vol%) or for 50 wt% Ti (~56 vol%), limiting metal loss by extrusion and/or reaction with the mold.

From the pressings conducted above and below liquification temperatures for various systems, it would appear that liquid phase sintering can be exploited if the amount of melt is small enough so as to prevent excessive mobility and reactivity. Two areas are indicated for further study: 1) preparation of TiC-C or ZrC-C with lower metal contents (20-30 wt%) and 2) fabrication of WC-C or MoC-C of higher metal contents (60-70 wt%), all in their liquid ranges. If the hypothesis concerning the effect of the volume of liquid present during fabrication is correct, such experiments should produce strong composites of TiC-C and ZrC-C and weaker bodies of WC-C and MoC-C.

Mechanical Properties - The room temperature strengths of the composites in the various systems (50 Ti-26, 50 V-26 and 50 W-30) were all quite high ($>10,000$ psi). However, no increase in strength was observed at 2000°C (Fig 28) and strong plastic deformation occurred at 2500°C . This high temperature behavior was similar to that for MoC-C but unlike the increase at 2000°C seen for NbC-C, TaC-C and ZrC-C.

A rather curious behavior was exhibited by the HfC-C composition. A slight increase in strength was evident at 2000°C for 65 Hf-30. Even higher strengths were measured for this composition at 2500°C although significant plastic deformation occurred. A 50 wt% Hf composite prepared in the first year's program displayed similar strength-temperature relationships. Data in the HfC-C system is insufficient at this time to explain this behavior.

From the various high temperature flexural strength measurements, it appears that strength and plasticity are a function of the liquification temperature of the particular system. The highest strengths and resistance to deformation at $\geq 2500^{\circ}\text{C}$ has been shown by TaC-C which exhibits the highest carbide-carbon eutectic. The second highest eutectic is that for NbC-C which also displays good structural integrity at the high temperatures. Systems having carbide-carbon eutectics or carbide melting points of less than 2800°C display no strength peak at 2000°C ; plastic deformation is already evident for these systems at this temperature.

G. Electrical Resistivity vs Strength

A linear strength - resistivity relationship has been found to hold true for metal carbide-graphite composite materials as illustrated in Figs 31-35. The relationship appears to hold regardless of density, processing temperature, wt% metal, grain direction, or carbon source for any particular system. This linearity indicates that strength is directly proportional to

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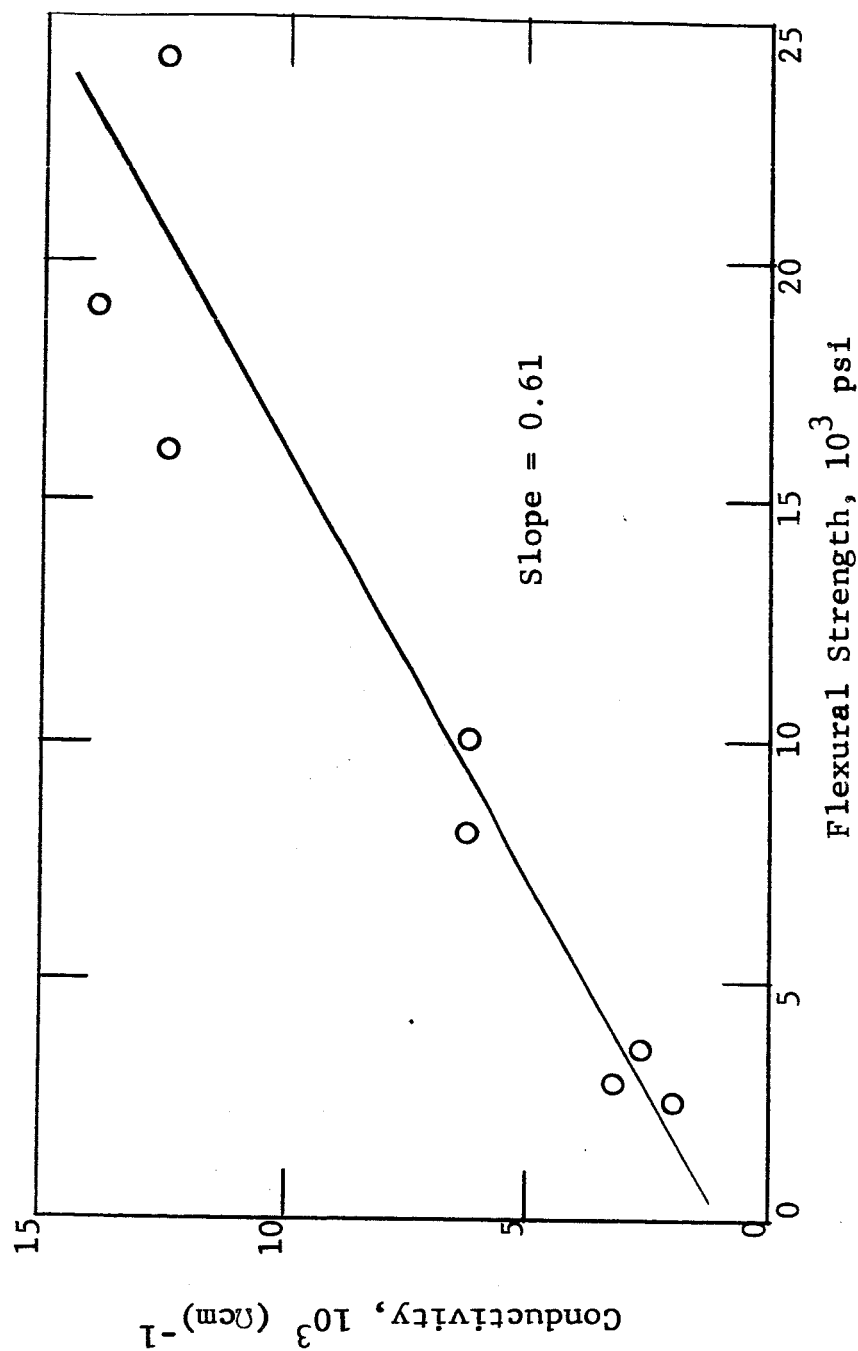


Fig 31 - ELECTRICAL CONDUCTIVITY AS A FUNCTION OF FLEXURAL STRENGTH FOR NIOBIUM-GRAPHITE COMPOSITES

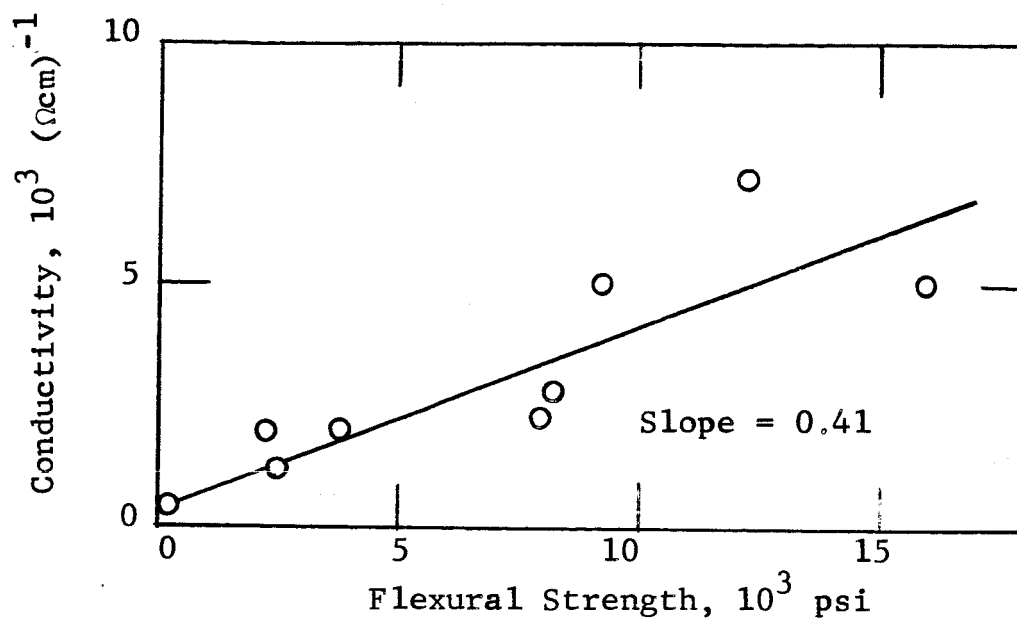


Fig 32 - ELECTRICAL CONDUCTIVITY AS A
FUNCTION OF FLEXURAL STRENGTH FOR
HAFNIUM-GRAPHITE COMPOSITES

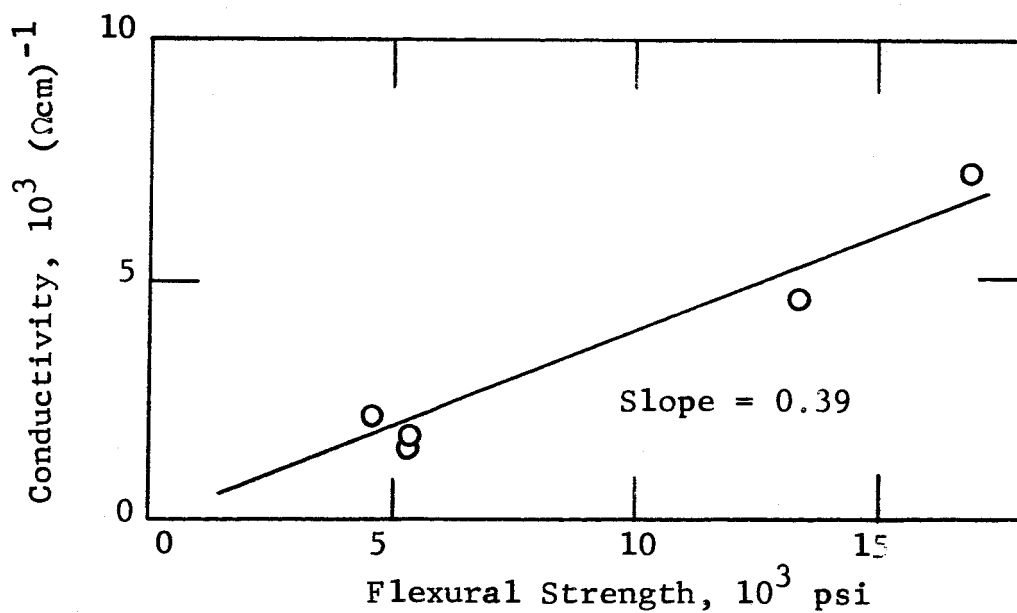


Fig 33 - ELECTRICAL CONDUCTIVITY AS A
FUNCTION OF FLEXURAL STRENGTH FOR
ZIRCONIUM-GRAPHITE COMPOSITES

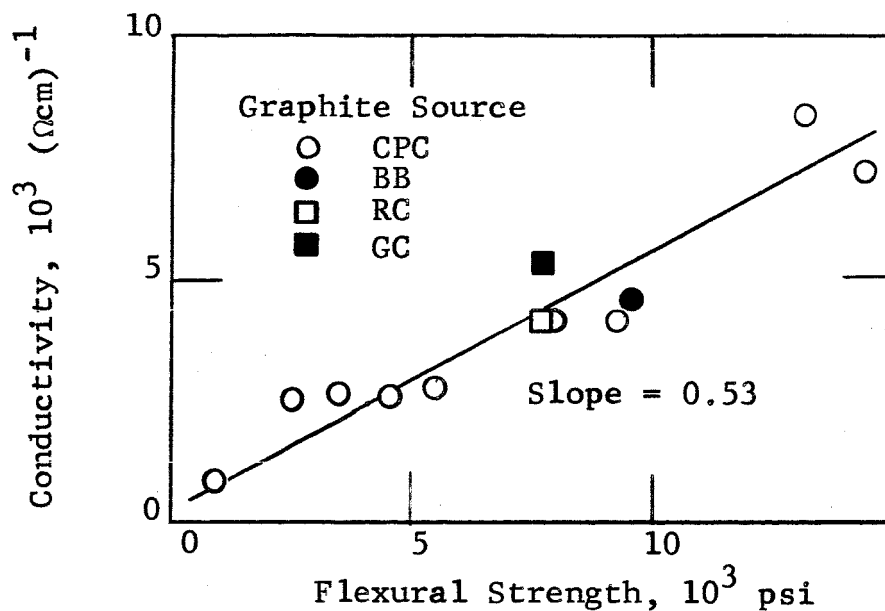


Fig 34 - ELECTRICAL CONDUCTIVITY AS A FUNCTION OF FLEXURAL STRENGTH FOR MOLYBDENUM-GRAPHITE COMPOSITES

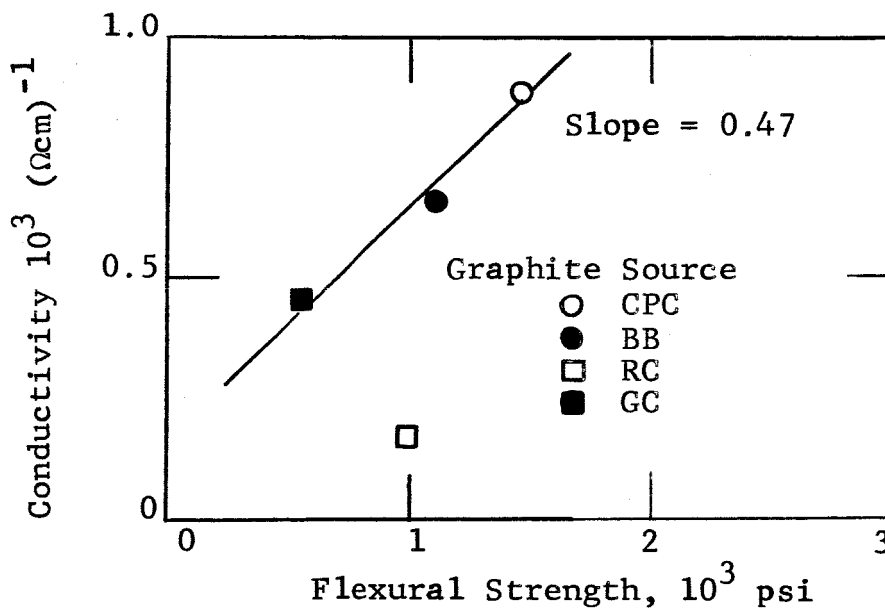


Fig 35 - ELECTRICAL CONDUCTIVITY AS A FUNCTION OF FLEXURAL STRENGTH FOR GRAPHITE BODIES

particle-to-particle contact of the carbide or eutectic which is the strength providing phase.

Knudsen¹² has given the explanation of the exponential relationship between mechanical strength and porosity in ceramic materials, which had been established on a semi-empirical base earlier by Ryshkewitch¹³ by showing that the effective contact area for any spatial arrangement of sphere like particle is a logarithmic function of the porosity. The porosity range within which this relation holds true depends on the packing structure and extends from 0 to about 40% porosity for a close packed cubic arrangement. Since the strength of a porous material is a linear function of the effective cross section, it follows that the strength also is a logarithmic function of porosity. It has also been verified experimentally by Rubin¹⁴ that the electrical resistivity of ceramic materials is an exponential function of the porosity for the same reason as in the above case. Thus, both strength and resistivity are linear functions of the effective cross section of a porous material which itself is a logarithmic function of the porosity. One would, therefore, expect a linear relationship between strength and electrical resistivity in single phase, ceramic materials. This relationship would no longer explicitly contain the porosity, and strength should be predictable from measurements of electrical resistivity independent of porosity.

It appears then that the highest possible strength obtainable in a particular composite system can be calculated from resistivity and strength measurements on two compositions, knowing the resistivity of the pure carbide. In this approach only the mechanically stronger phase, which is also the electrically better conducting phase, was considered and the graphite phase together with physical voids were treated as porosity. The slope of the conductivity-strength relationship, which is close to 0.5 for the systems studied, is considered to provide a

sensitive measure of the strengthening mechanism in these composite systems and should reflect the effect of processing conditions on the microstructure.

H. Thermal Shock Studies

Preliminary experiments were conducted to examine resistance to thermal shock of various composites. During the test, temperatures of greater than 3000°C was achieved at the test tip of the sample within 20 sec. On subsequent cycles, this temperature was reached in 15 sec. On the off cycles, cooling to below 800°C was accomplished within 10 sec.

These early tests indicate that the metal carbide-graphite composites have good resistance to thermal shock. No failure due to cracking occurred in any of the samples. Compositions which were subjected to this test include tantalum, niobium and zirconium bodies; in addition, ATJ graphite test bars were subjected to this test. The attainment of very high temperatures (>3250°C) as monitored by an L & N optical pyrometer was verified by the fact that both niobium and zirconium composites underwent melting; tantalum composites did not show such melting, indicating that the highest temperature was in the range of 3250° - 3450°C.

Improvements in testing technique will be incorporated prior to any further testing. Some difficulty was encountered in torch alignment, and some slight oxidation prevented accurate data gathering as to dimensional and weight changes. Pure carbide materials which are known to have poor thermal shock resistance will be obtained for comparative evaluation.

Efforts will also be made to use different types of thermal shock tests. The present test involves small samples and altho thermal gradients are induced in the longitudinal axis, radial gradients are quite limited. Experiments in which

discs are thermally stressed in the center resulting in strong radial gradients to the periphery will be used.

IV. FUTURE WORK

The continuation of the present work will have a two-fold purpose. Engineering data for anticipated hardware applications will be obtained, while basic studies will generate additional information for developing a better understanding of carbide-graphite composites.

The work will be primarily concerned with determination and evaluation of the mechanical and physical properties of the most promising compositions in the TaC-C, NbC-C, and HfC-C systems. Behavior of these compositions under flexural, compressive or tensile stresses, and thermal expansion and conductivity will be examined at temperatures up to 3000°C.

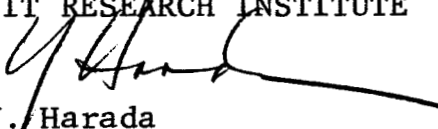
In addition, the ZrC-C and Mo₂C-C systems will receive some study. The zirconium compositions are of interest as potential high temperature materials which are only slightly less refractory than the above mentioned systems. Molybdenum studies will help in the study of graphitization mechanisms. Ternary systems such as Ta-Zr-C and Ta-Nb-C will receive preliminary evaluation. Along with the compositional investigations, the effects of different raw materials and fabrication parameters will be determined.

V. CONTRIBUTING PERSONNEL AND LOGBOOK RECORD

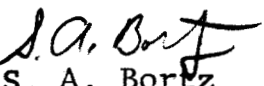
The following personnel have participated in this research program: S. A. Bortz, G. A. Rubin, Y. Harada, R. Baker and D. L. Berent. All data pertaining to this project are recorded in IITRI Logbook Nos. C16005, C16010, C16483, C16487, C16500, C16802, C16806, C16816, C16973 and C16974.

Respectfully submitted,

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